High energy X-ray absorption spectroscopy: Current status and future applications

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Workshop on
"Science with High-Energy X-rays"
August 9-10 , 2004, APS, Argonne, Illinois

Overview

X-ray absorption

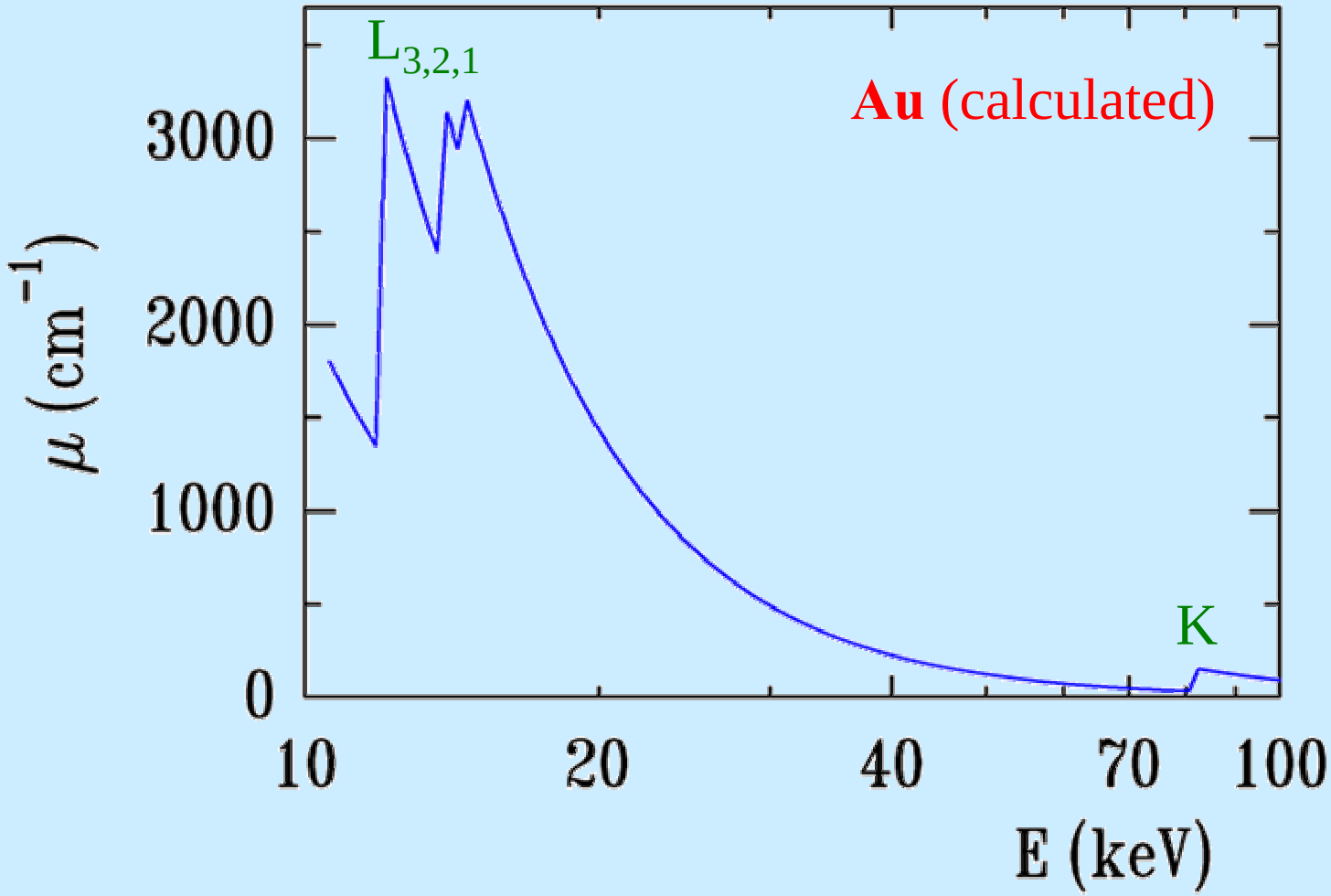
- Principles of XANES und EXAFS
- Edge positions of K- and L-edges
- Lifetime broadening – and how to get rid of it

Applications

- Metals
- Melting
- Time resolution
- Tomography
- Beamline layout at PETRA

Conclusions

X-ray absorption edges



$_{79}$Au

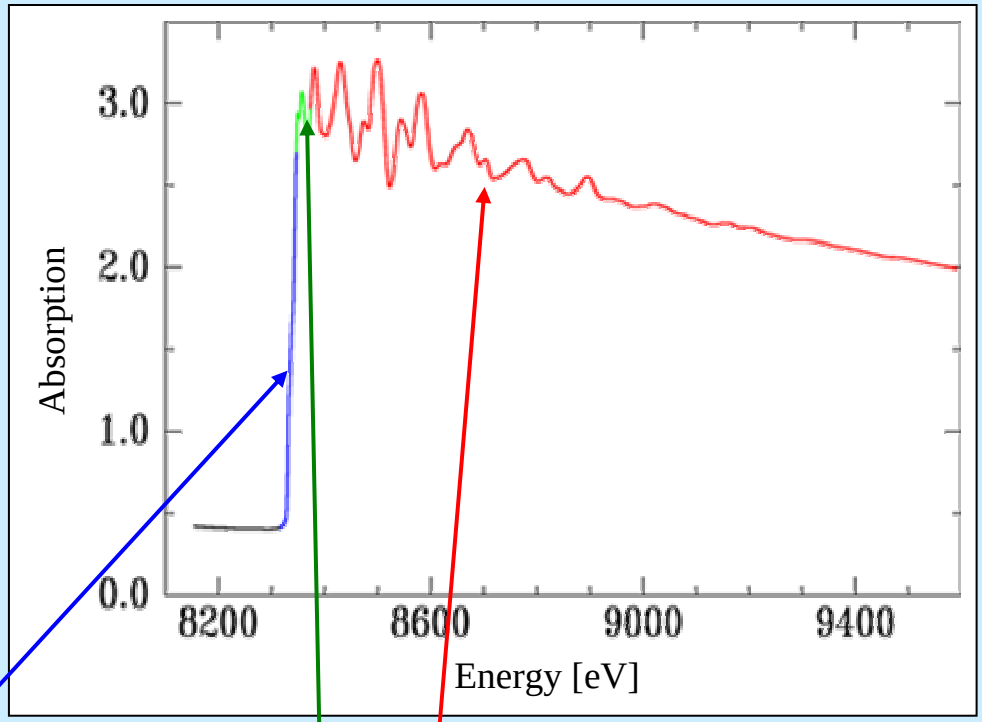
K: 80.725 keV

L_3: 11.919 keV

L_2: 13.734 keV

L_1: 14.353 keV

Absorption spectra of a Ni-metal foil



Absorption edge ⇒ **Valence of the absorbing atom**

Near edge region (XANES) ⇒ **Bond angles**
⇒ **„Fingerprinting“**

Extended edge region (EXAFS) ⇒ **Interatomic distances**
⇒ **Coordination number**
⇒ **Identification of the neighbour atoms**

Theoretical description of the EXAFS

K-edges, single gaussian pair distribution of neighboring atoms:

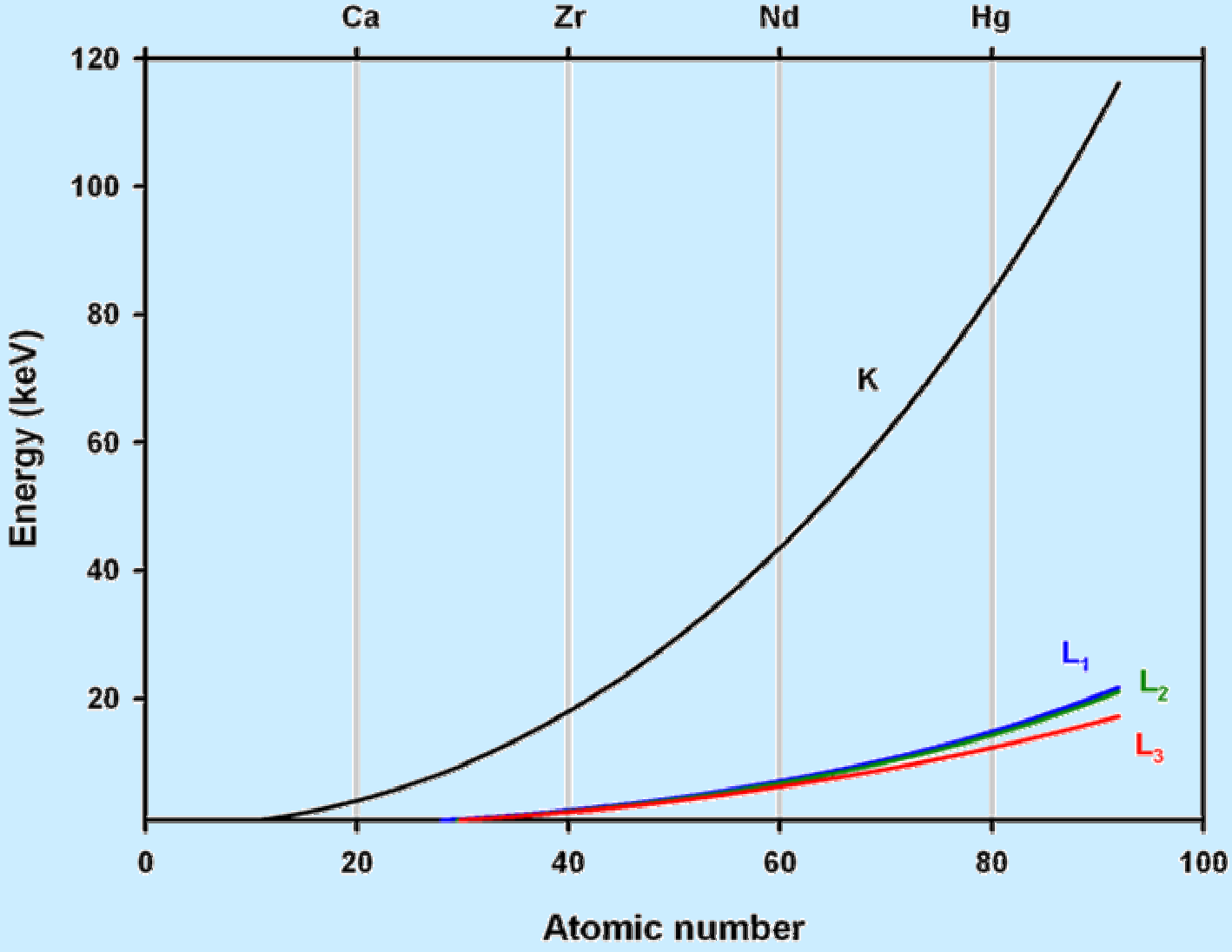
$$\chi(k) = -\tfrac{1}{k} A(k) \cdot \sin\left[2kr + \Phi\left(k\right)\right]$$

where

$$A(k) = \frac{N}{r^2} \left| f\left(\pi, k\right) \right| e^{-2r/\lambda} e^{-2\sigma^2 k^2}$$

k	**wavenumber of photoelectrons**
r	**average atomic distance**
ϕ(k)	**scattering phase due to potentials of central atom (ϕA) and backscattering atom (ϕB), $\phi = \phi A + \phi B$**
N	**coordination number**
$\lvert f(\pi, k) \rvert$	**backscattering amplitude**
λ	**mean free path of photoelectrons**
σ	**Debye-Waller-factor**

Edge energies



What are „high energy absorption edges“?

Heaviest tabulated element:

$_{100}$Fm	K	141.930 keV
	L_1	27.573 keV
	L_2	26.644 keV
	L_3	20.868 keV

R.D. Deslattes et al.,
Rev. Mod. Phys. 75, 35 (2003)

⇒ Above 30 keV only K-edges, > $_{51}$Sb (E_K=30.491 keV)

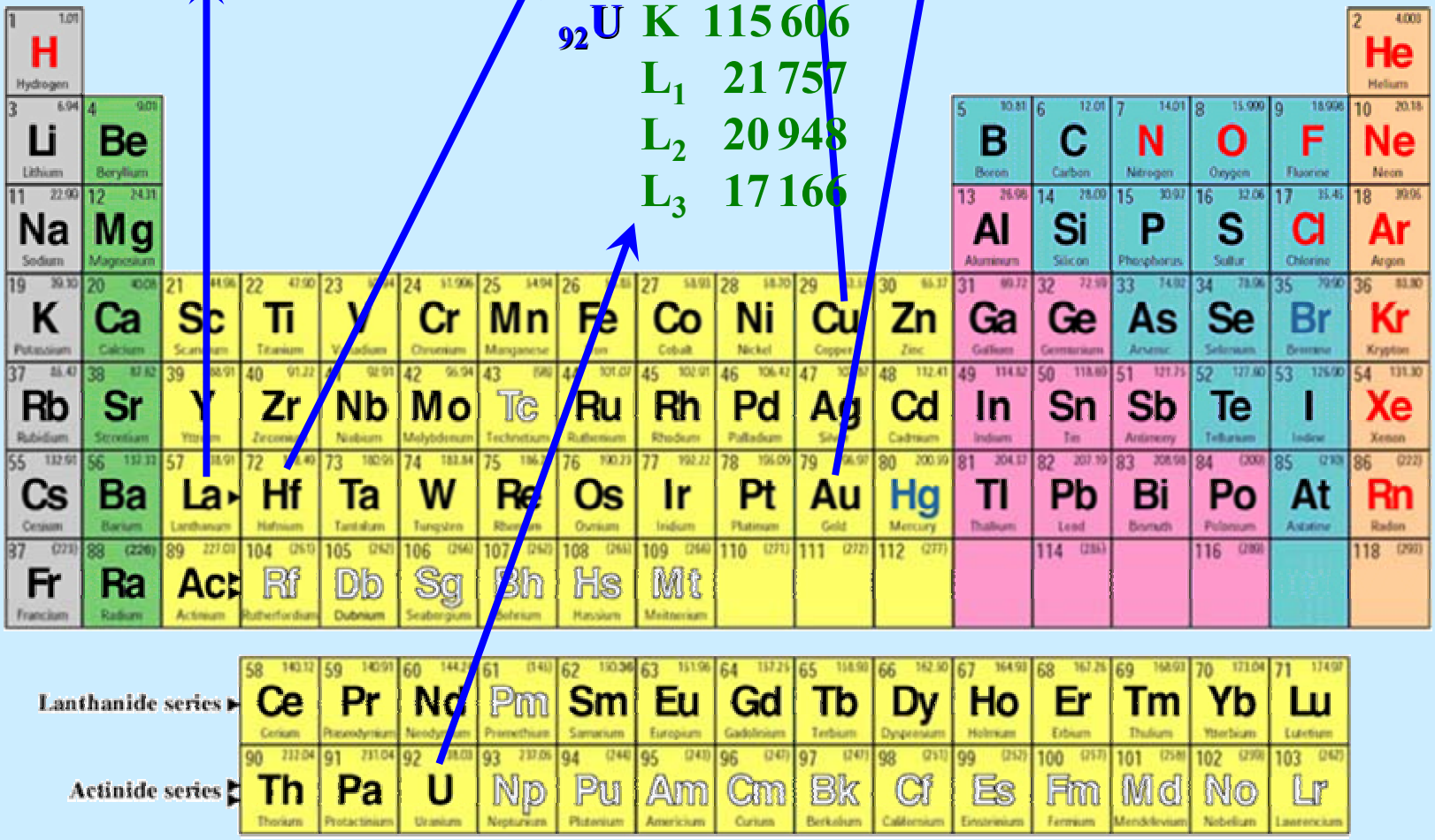
Advantages of K-edges:

- Only one (primary) final state (p-state)
- No overlap with other edges
- Polarization dependent measurements:
  Final state has simple p-symmetry

Edge energies in eV

$_{57}$La	K	38 925	$_{72}$Hf	K	65 351	$_{29}$Cu	K	8 979	$_{79}$Au	K	80 725
	L_1	6 266		L_1	11 271		L_1	1 096.7		L_1	14 353
	L_2	5 891		L_2	10 739		L_2	952.3		L_2	13 734
	L_3	5 483		L_3	9 561		L_3	932.7		L_3	11 919

$_{92}$U K 115 606
L_1 21 757
L_2 20 948
L_3 17 166



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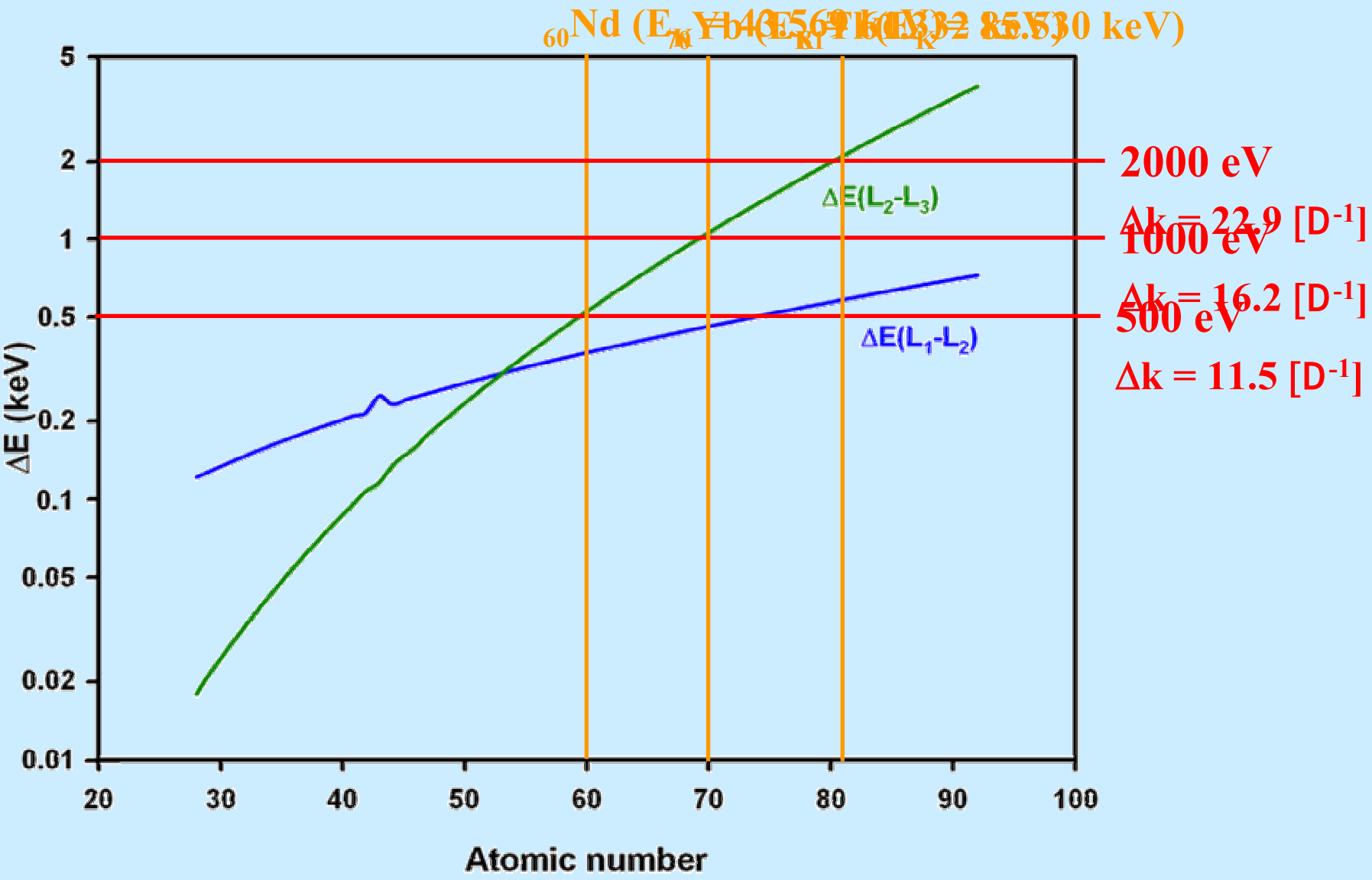
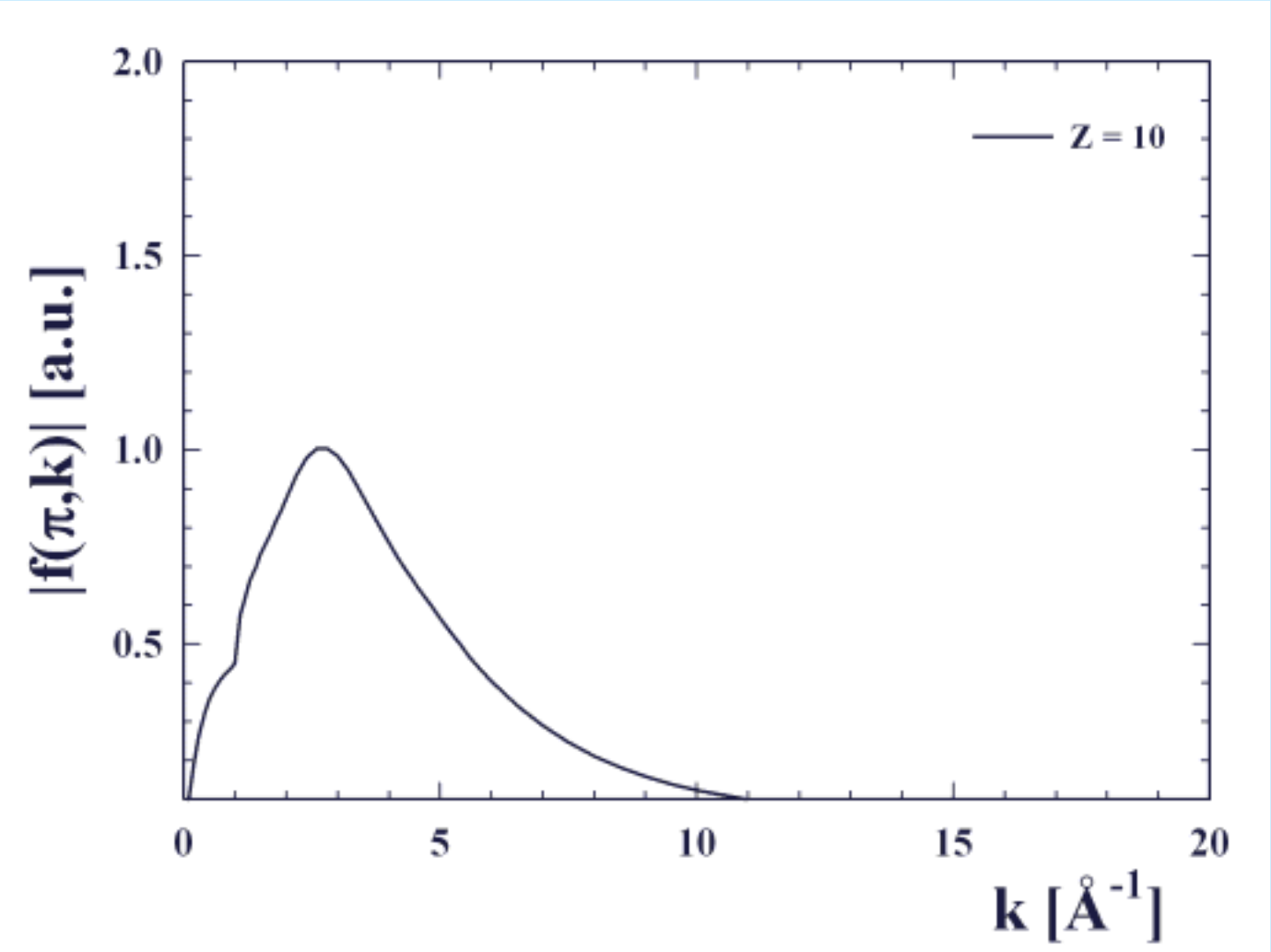
EXAFS ranges at L_3- and L_2-edges



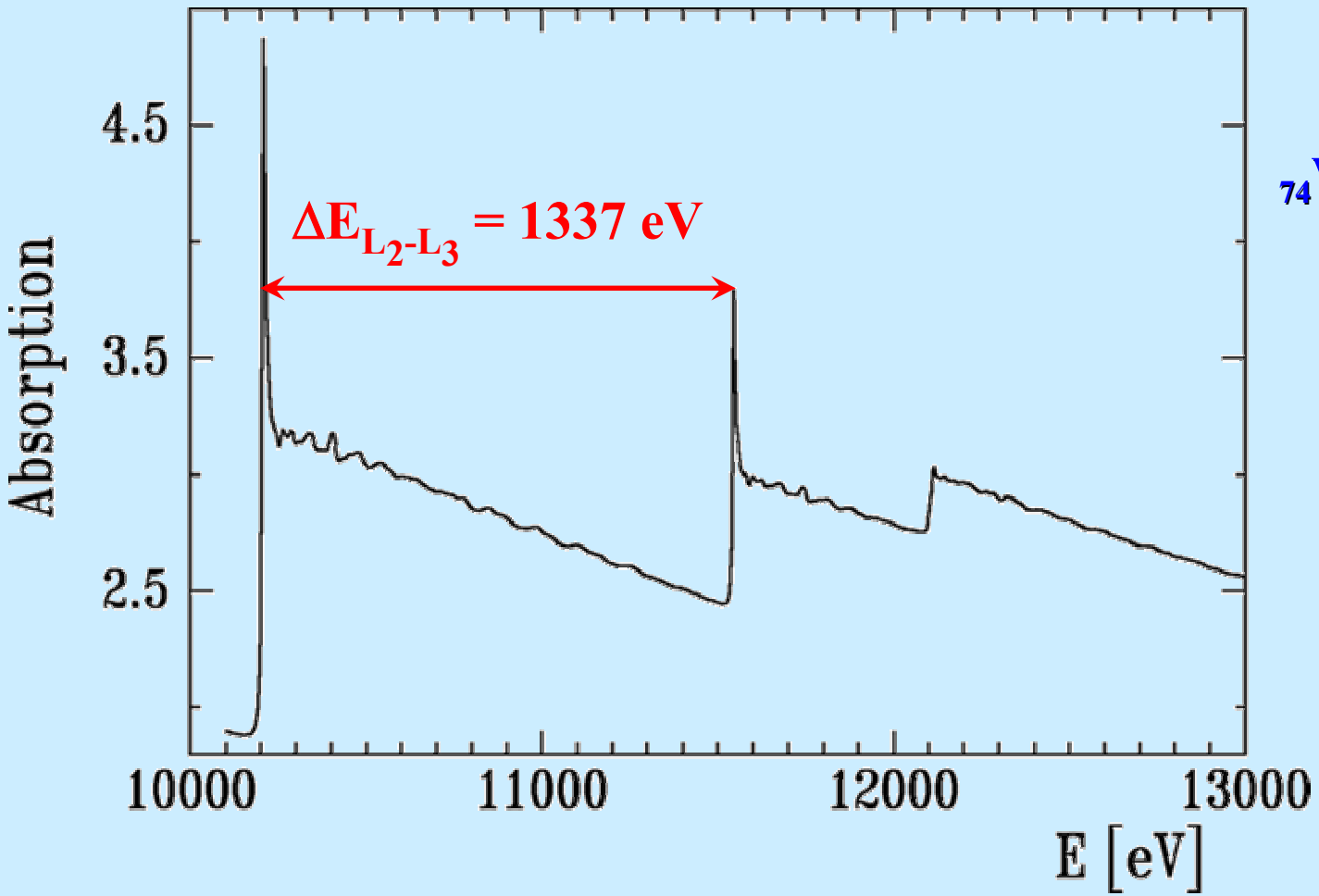
Backscattering amplitudes



BSAs for Z = 10 - 90

Calculated with FEFF-program

Wide energy range: W L-edges

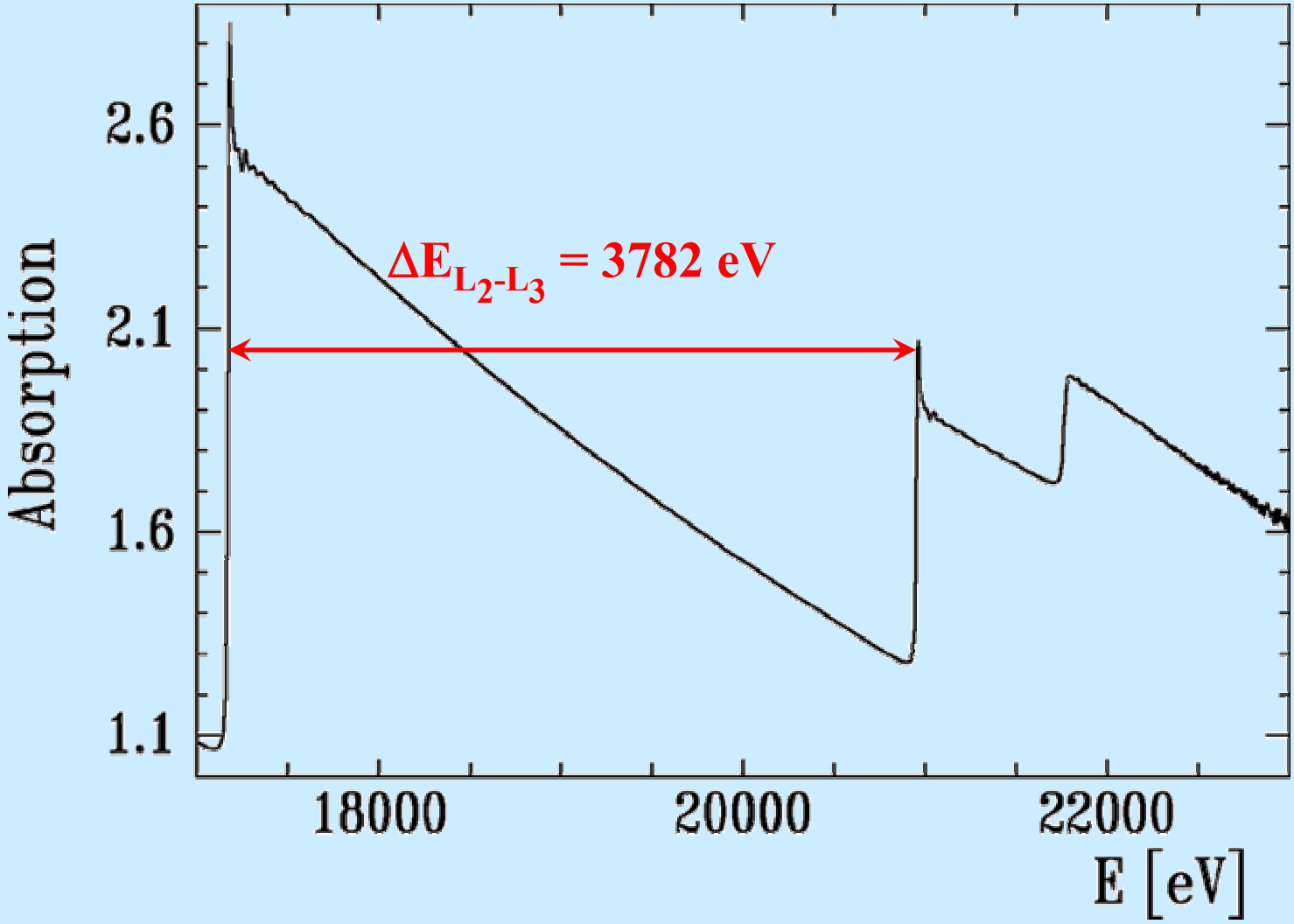


$_{74}$W	K	69 525 eV
	L_1	12 100 eV
	L_2	11 544 eV
	L_3	10 207 eV

W powder (300 K), 40.8 s (0.02 s / point)

X-11A at the NSLS

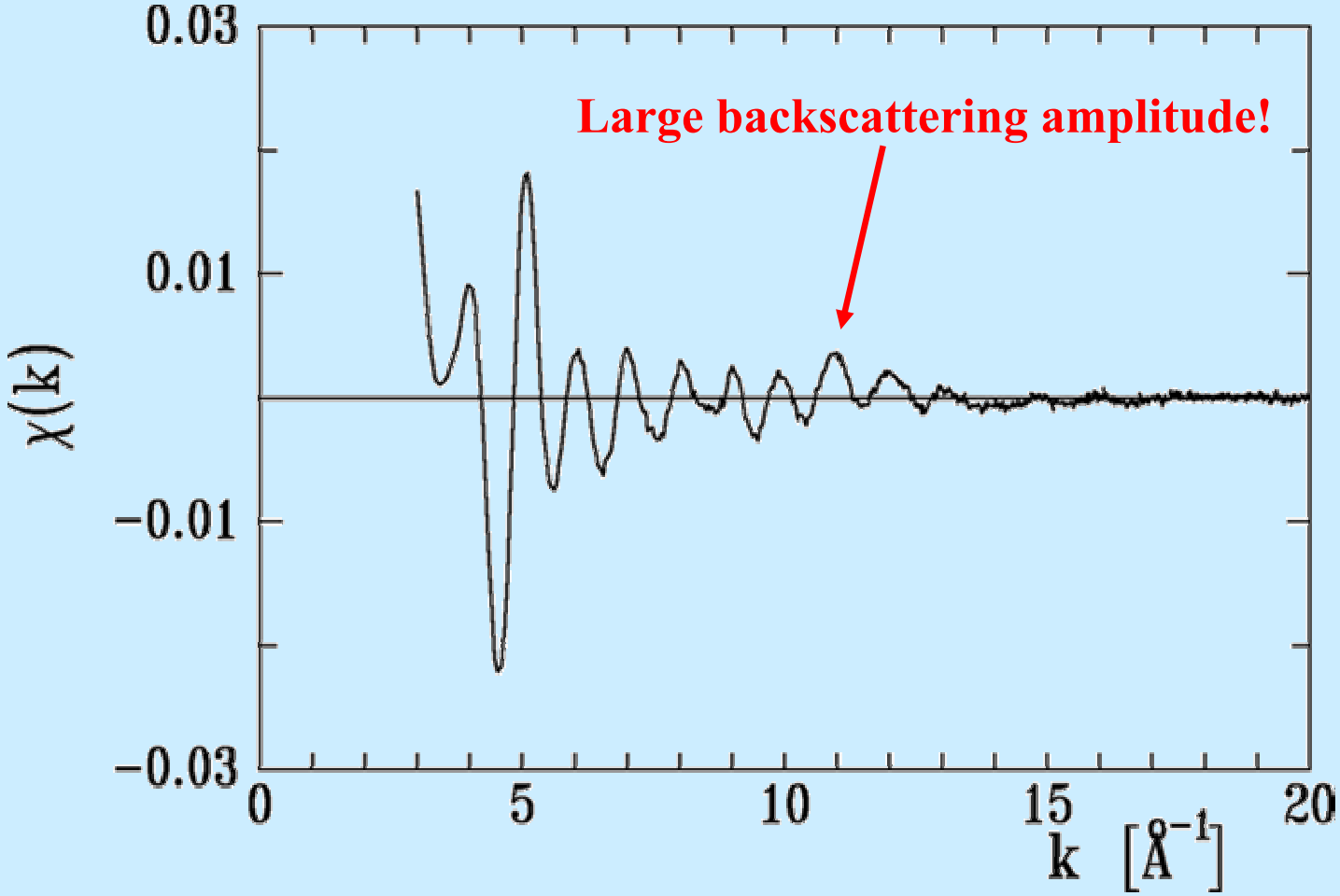
Extreme energy range: U L-edges



$_{92}$U	K	115 606
	L_1	21 757
	L_2	20 948
	L_3	17 166

U L-edges, 115 s (0.05 s / point)

Extreme energy range: U L-edges



U L_3-EXAFS

Δk=31.5 Å^{-1} possible!

EXAFS / XANES of heavy elements

EXAFS:

⇒ For good EXAFS-measurements (1 keV range).
K-edges up to ≈ $_{70}$Yb (E_K = 61.332 keV) necessary.

What about heavier elements like $_{92}$U?

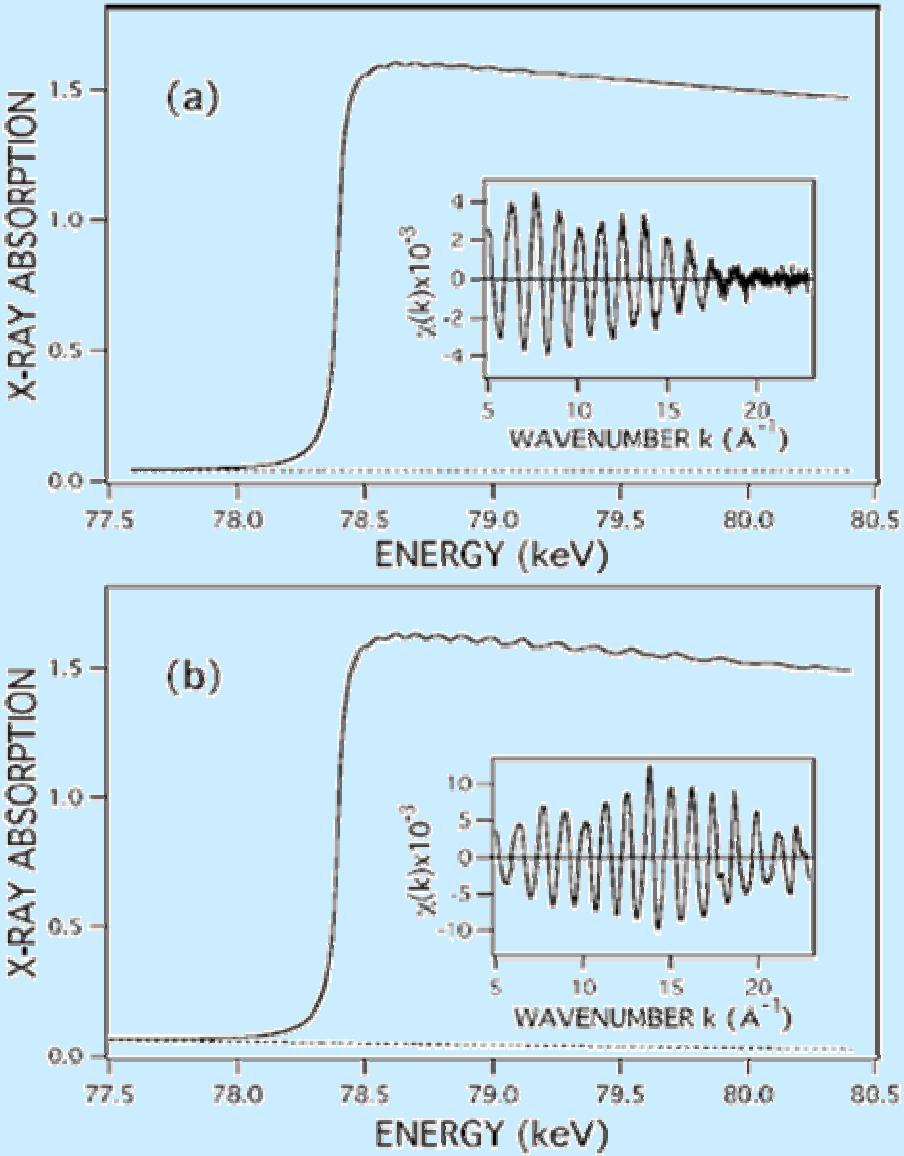
L-edges overlap with K-edges of common materials,
e.g. Pu in Zircon (ZrSiO4).

K-edges of neigbouring heavy elements do not overlap, L-edges do!
$_{92}$U/$_{91}$Pa: ΔE_K = 3005 eV, ΔE_{L3} = 433 eV.

XANES:

L-edges can usually be measured.

Pt K-edge



Pt-foil

Room temperature (299 K)

12 K

Y. Nishihata et al., J. Synchrotron Rad. 8, 294 (2001)

Lifetime broadening

Heisenberg's uncertainty relation:

$$\Delta t \Delta E \geq \hbar/2, \hbar = 6.6 \cdot 10^{-16}\ [\mathrm{eV \cdot s}]$$

Limited lifetime of vacancy $\Rightarrow$ energy broadening of the edge

Modification of EXAFS-formula:

Convolution with Lorentzian function with width Γ:

$$\chi(E)=\chi_0(E)*g(E,\Gamma_K)$$

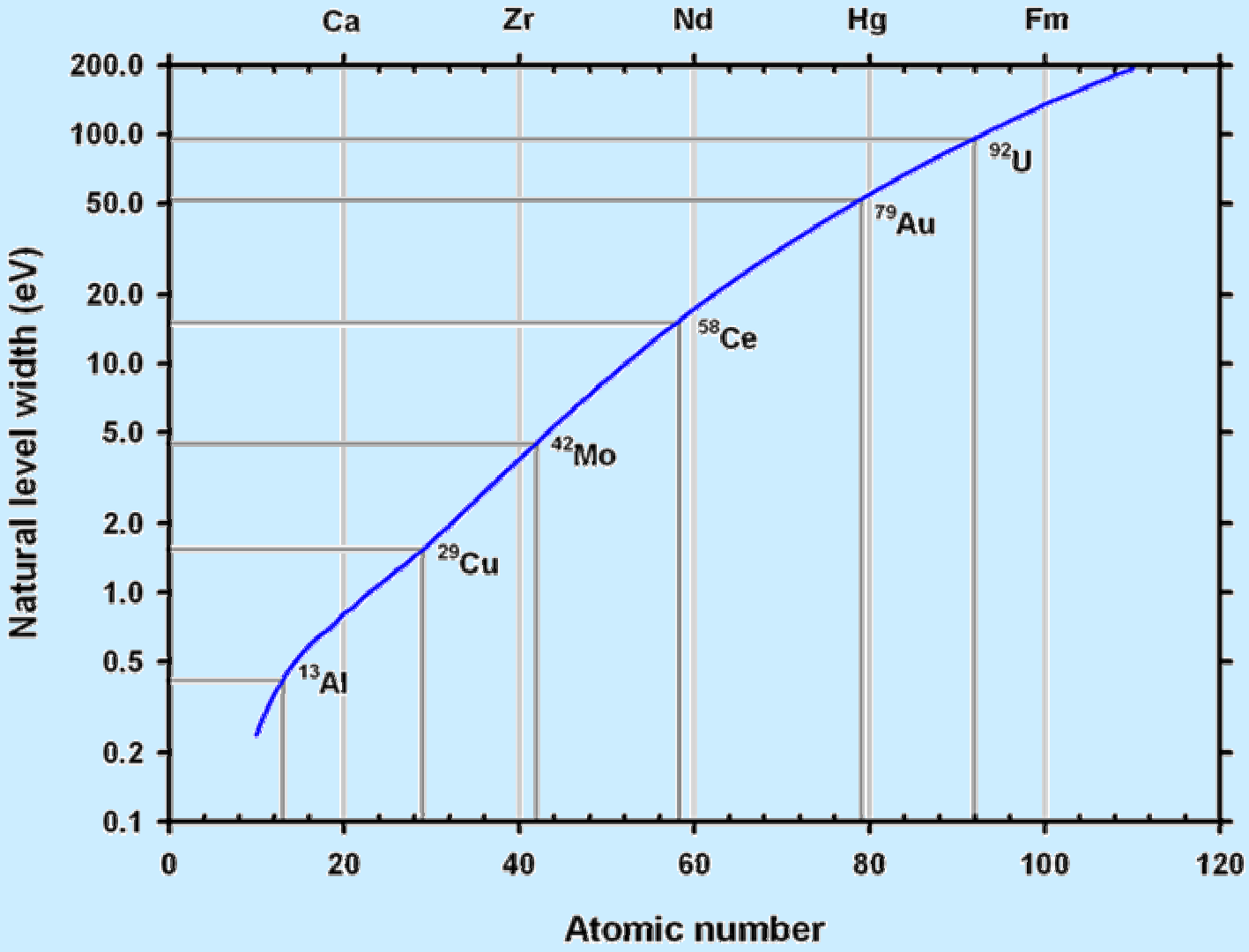
Finite lifetime modifies amplitudes *and* phases of the EXAFS

[D.G. Stearns, Phil. Mag. B 49, 541 (1984)]

Tabulations of experimental and theoretical lifetime broadening:

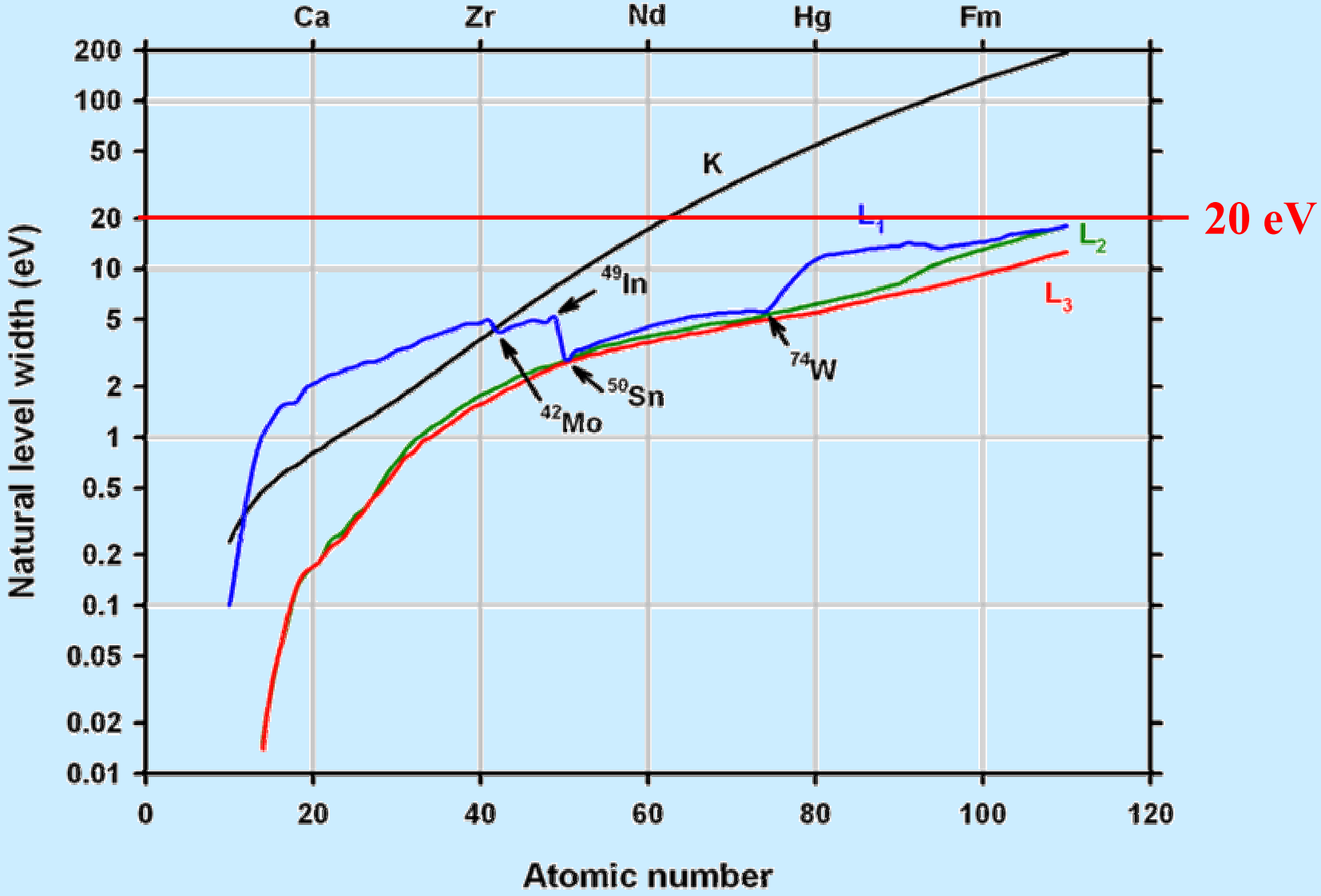
M.O. Krause and J.H. Oliver, J. Phys. Chem. Ref. Data **8,** 329 (1979)

Natural edge widths of the K-shell



M.O. Krause and J.H. Oliver, J. Phys. Chem. Ref. Data 8, 329 (1979)

Natural edge widths of K- and L-shells



M.O. Krause and J.H. Oliver, J. Phys. Chem. Ref. Data 8, 329 (1979)

Numerical deconvolution of the lifetime broadening

Convolution theorem of Fourier-transforms:

$FT\{f * g\} = FT(f) \cdot FT(g) \quad \Rightarrow \quad f = FT^{-1}\{FT(f * g) / FT(g)\}$

Lifetime broadening:

Convolution with Lorentzian function, FWHM Γ, HWHM $\Gamma' = \Gamma/2$.

Lorentzian: $L(x) = \frac{1}{\pi\Gamma'} \frac{1}{1 + (x/\Gamma')^2}$

$\Rightarrow \qquad FT\{L(x)\} = \tilde{L}(q) = \exp(-\Gamma'|q|)$

$\Rightarrow$ **Deconvolution in Fourier space:** Multiplication with $\exp(+\Gamma'|q|)$

$\Rightarrow$ Numerical deconvolution: Needs VERY good, low noise data.

A. Filipponi, J. Phys. B: At. Mol. Opt. Phys. 33, 2835 (2000)

Numerical deconvolution of the lifetime broadening

A. Filipponi, J. Phys. B: At. Mol. Opt. Phys. 33, 2835 (2000)

Decomposition of measured spectrum $\alpha(E)$ into three components:

$$\alpha(E) = (aE + b) + S(E) + \beta(E)$$

Linear pre-edge background

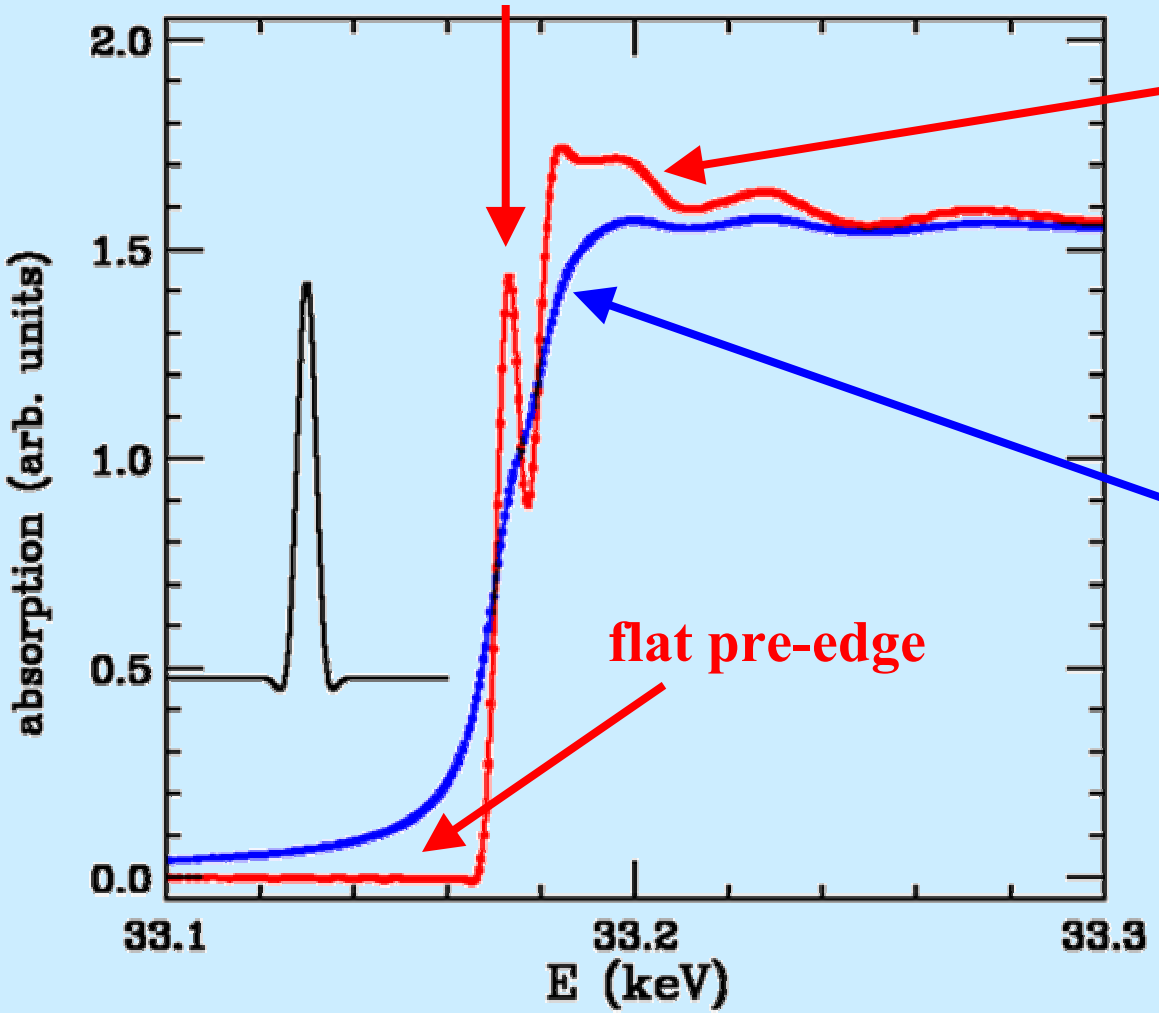
Step function representing edge

⇒Oscillating function with smooth decays to 0 at both ends
⇒ Suitable for FT

During deconvolution:

unaffected / **analytically solved** / **numerically deconvolved**

Numerical deconvolution: I K-edge



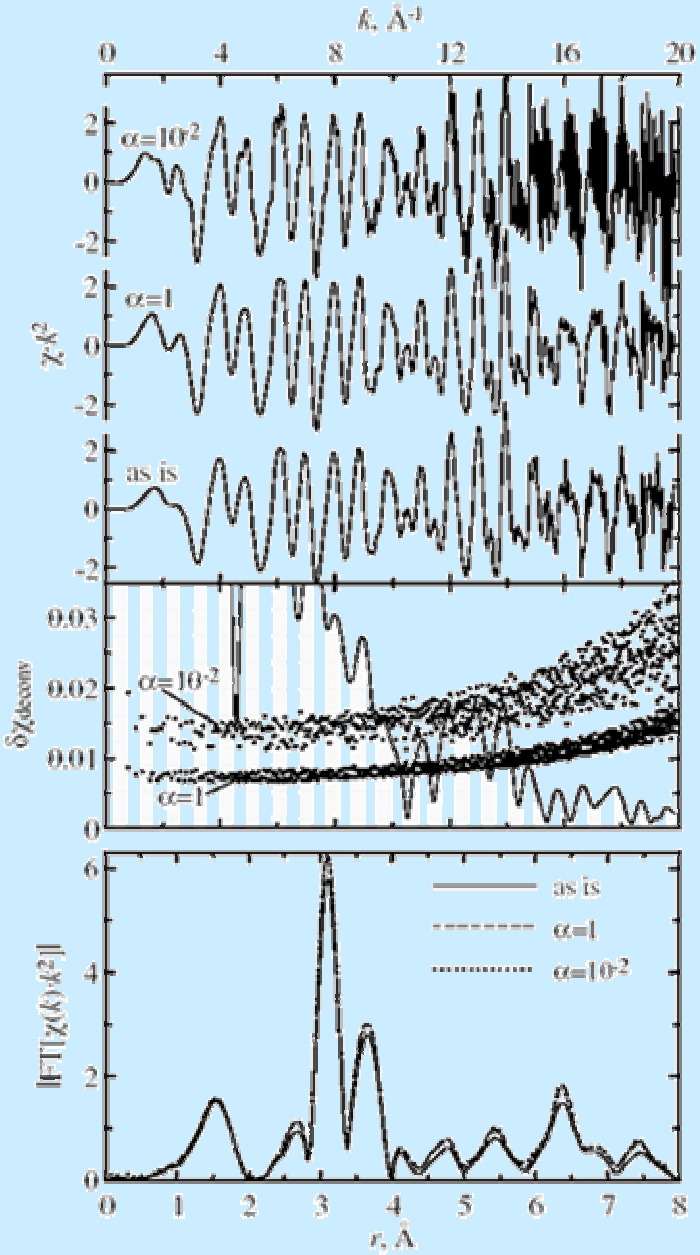
I_2 gas, K-edge

$E_K = 33.169$ keV

$\Gamma_{FWHM} = 10.6$ eV

A. Filipponi, J. Phys. B: At. Mol. Opt. Phys. 33, 2835 (2000)

Numerical deconvolution



K.V. Klementev, J. Phys. D: Appl. Phys. 34, 2241 (2001)

In deconvolution there is usually not a unique solution.

However:

Klementev uses Bayesian deconvolution.

For EXAFS: The deconvolved results give very similar FTs

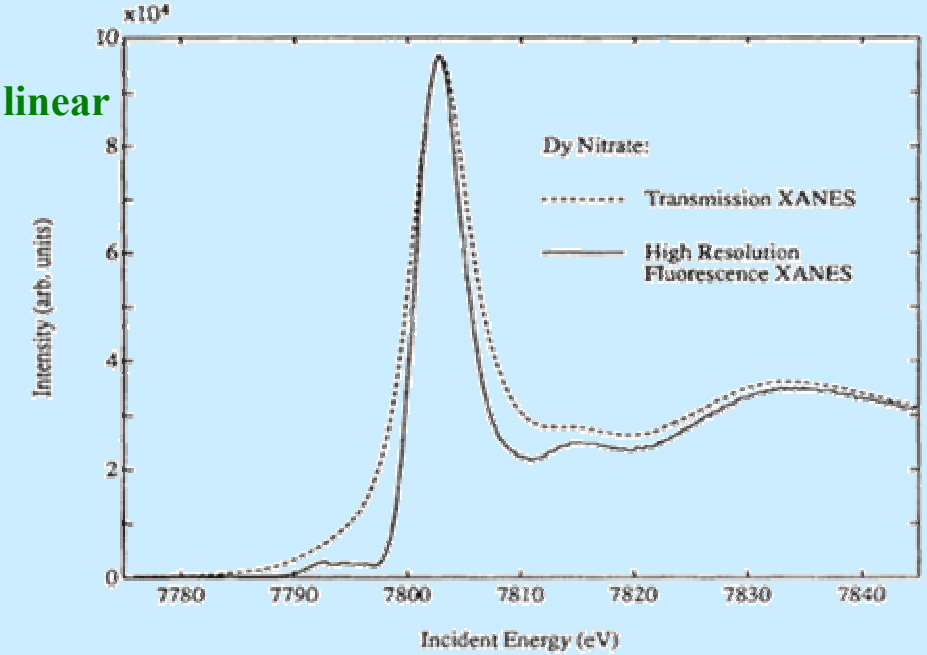
Experimental elimination of lifetime broadening

K. Hämäläinen et al., Phys. Rev. Lett. 67, 2850 (1991)

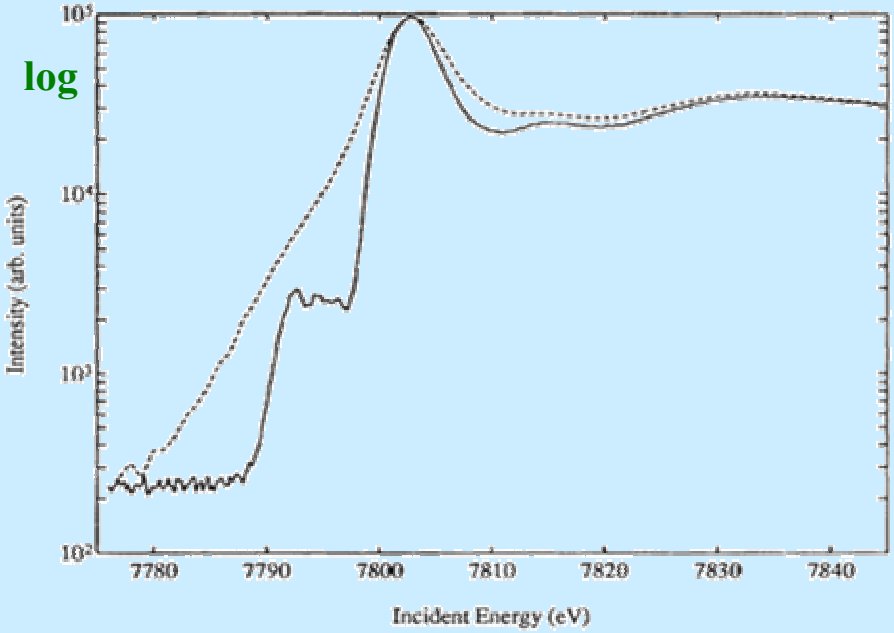
Prerequisites:

- High resolution monochromator (<Γ), here: Si(220): 0,7 eV.
- Sharp secondary channel (fluorescence, Auger) + high resolution analyser (<Γ), here: Si(440), 0.3 eV.

linear



log

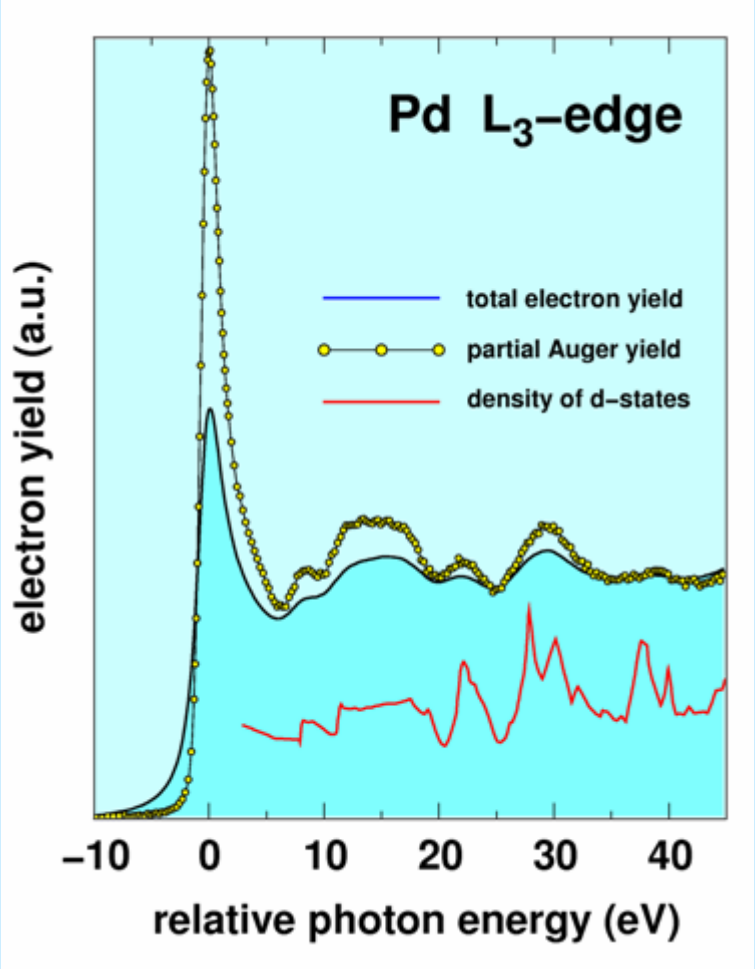


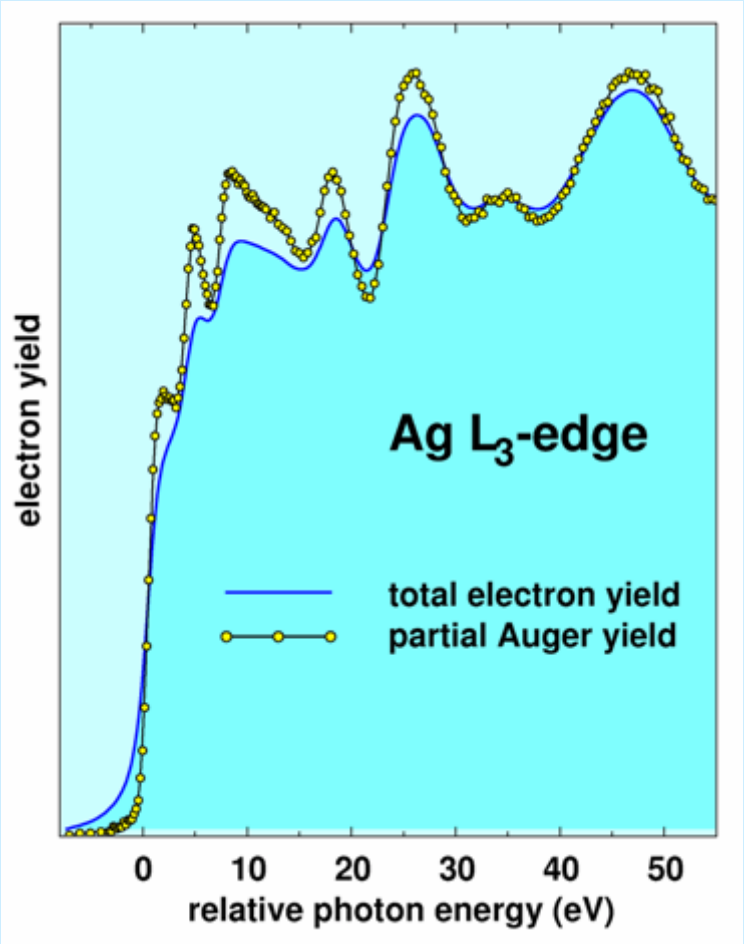
$_{66}$Dy L_3-edge in $Dy(NO_3)_3$

Γ_{L3} = 4.17 eV, $L_{\alpha 1}$-line: E_{M5}-E_{L3}=6495 eV, Γ_{M5} = 1.4 eV

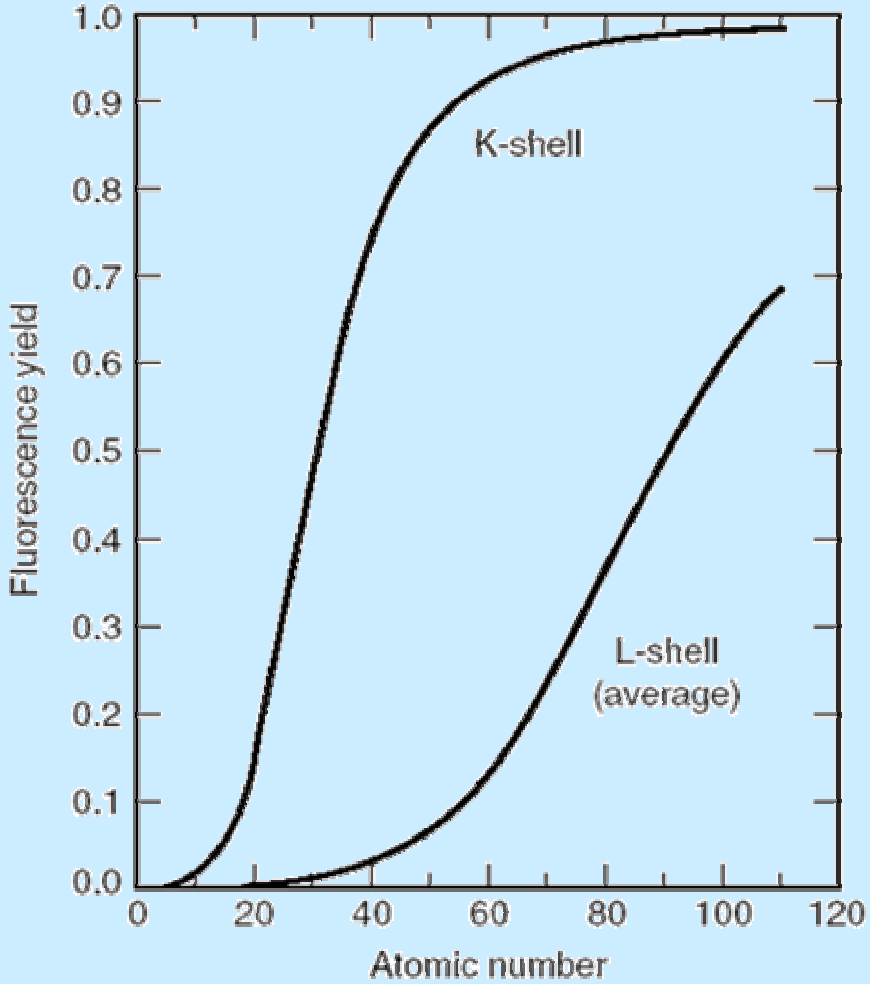
Constant final state X-ray absorption: Sub-lifetime near edge structure

W. Drube, HASYLAB





Fluorescence yields for K- and L-shells



Probability of radiative processes increases with atomic number:

> 80% from $_{45}$Rh
> 90% from $_{56}$Ba

M.O. Krause, J. Phys. Chem. Ref. Data 8, 307 (1979)

Conclusions: Removing the lifetime effect

First step:
Experimental "sharpening" via intermediate states:
Based on narrower intermediate states with longer lifetimes
($L_{2,3}$ for K-absorption, $M_{4,5}$ for L_3-absorption etc.) than the hole level.

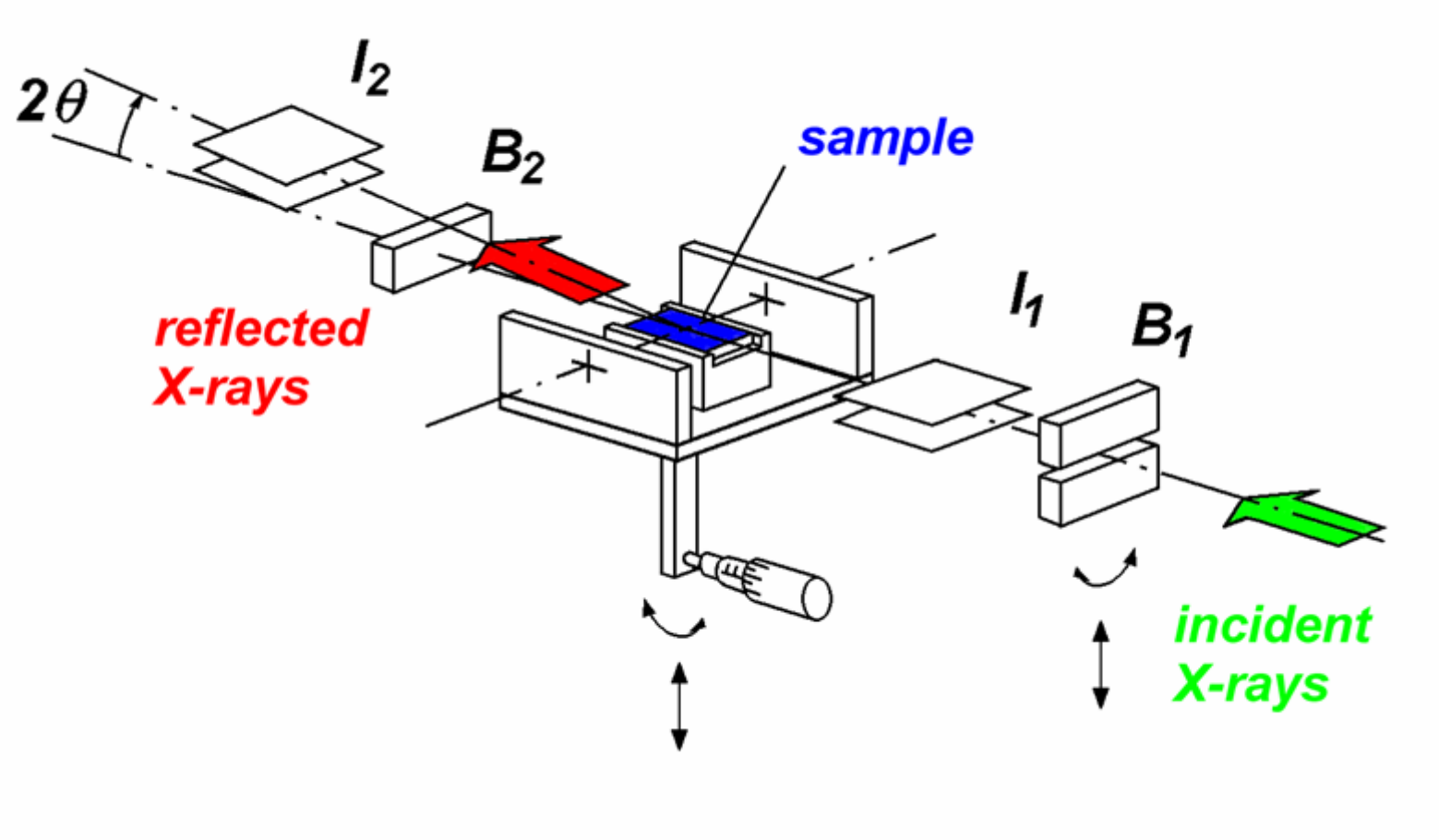
They differ by a factor of 3 to 8 to K-levels.

$\Rightarrow$ In principle the edge width can be reduced down to the width of the intermediate state,
e.g. for the Pt K-edge from about 49eV down to 6eV.

Second step: Numerical deconvolution of remaining width.

However: High resolution analyser necessary!
The same it true for resonant inelastic X-ray scattering (RIXS) methods.

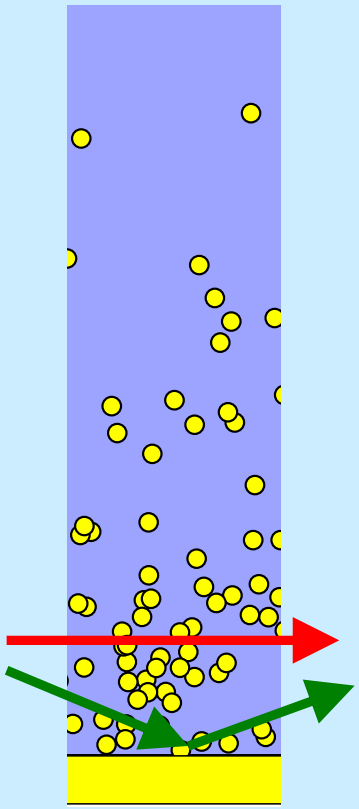
EXAFS measurements in reflectivity



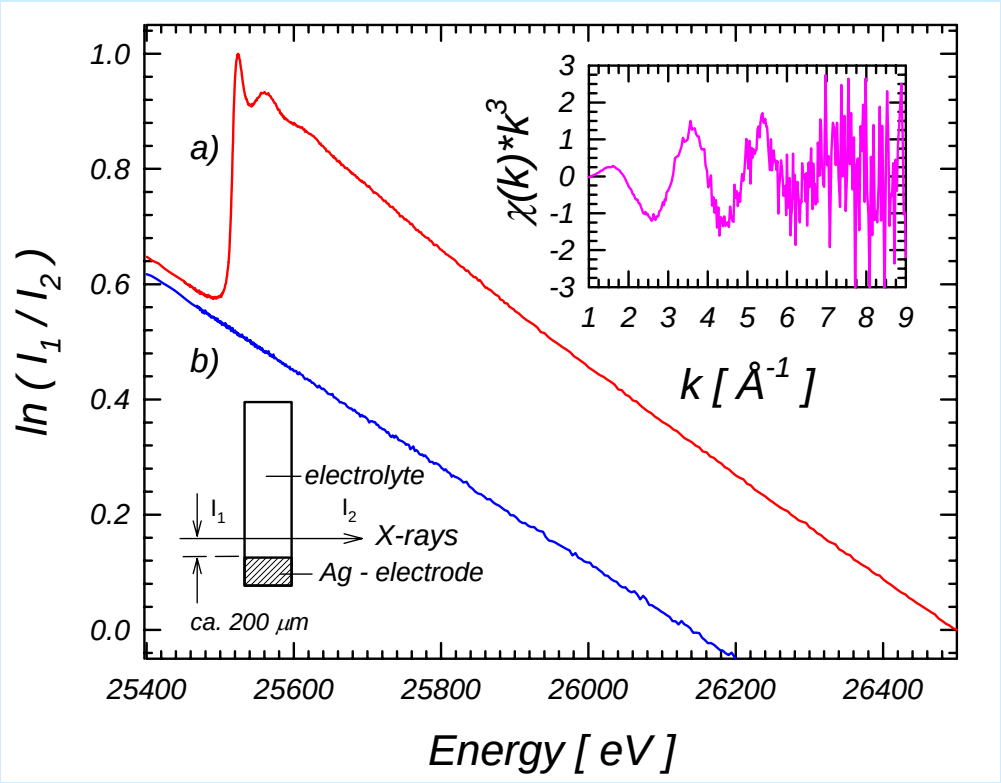
Experiment

Intrinsic surface sensitivity, depth profiling possible

Corrosion processes: Ag in Na_2SO_4 (pH 6.5)



- Material is released to the liquid phase.

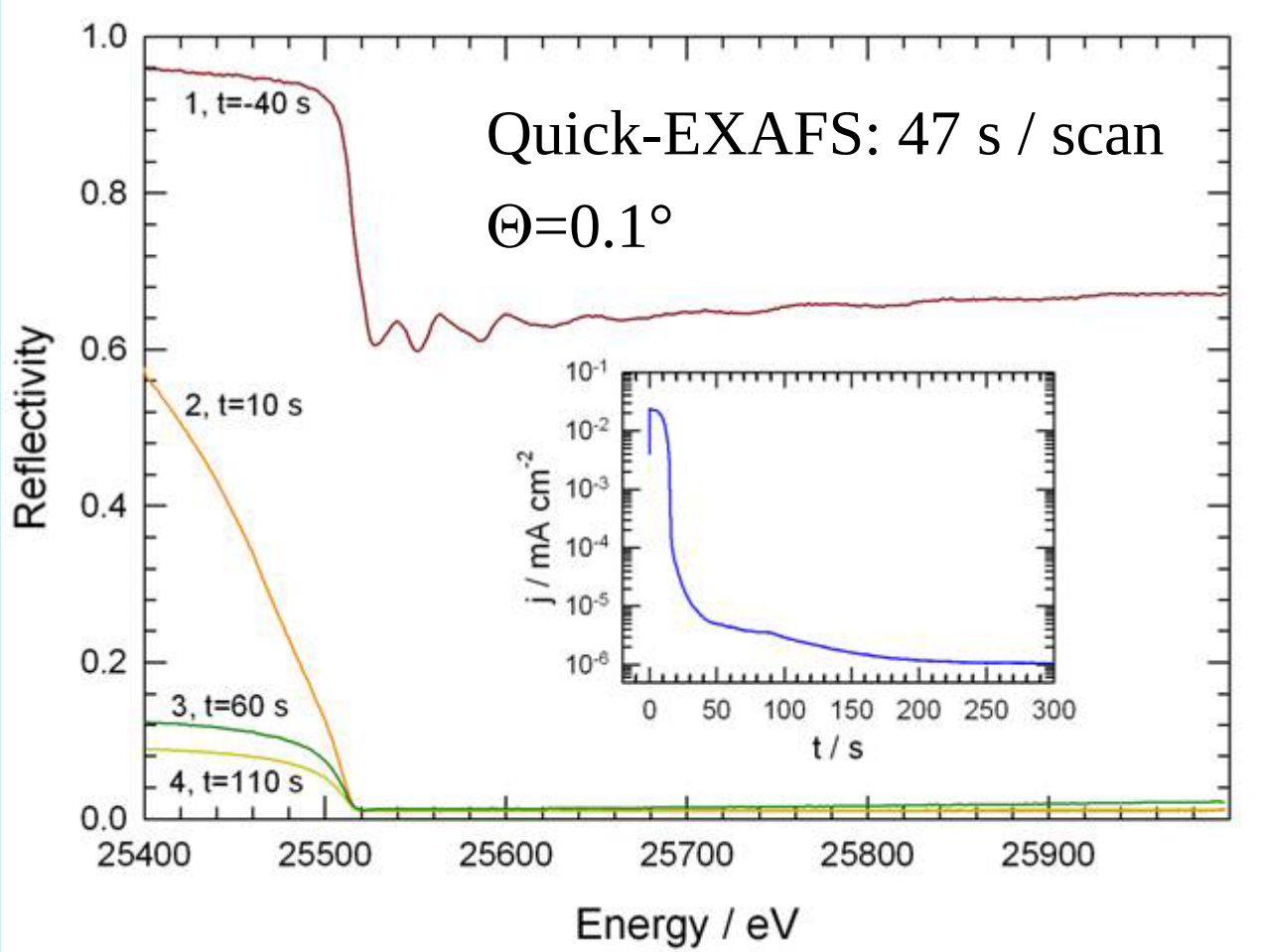


a) 0.5M Na_2SO_4
U=+1.20 V

b) 1M NaOH
U=+1.1 V

- Formation of $Ag(OH)_2^-$ in solution
- State of the surface?
- Formation of (partly) passive layers?

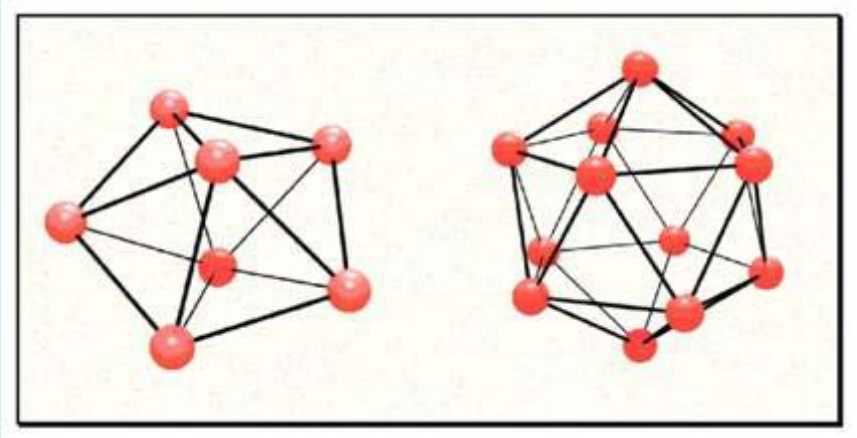
Corrosion processes: Ag in Na_2SO_4 (pH 6.5)



Dramatic reflectivity changes!

High energy XRD

5-fold symmetries in liquids (e.g. liquid Pb)



Contact of liquid with crystalline surface, e.g. liquid Pb / Si (100):

Local structure at the „buried“ interface?

Hard to investigate with conventional techniques:

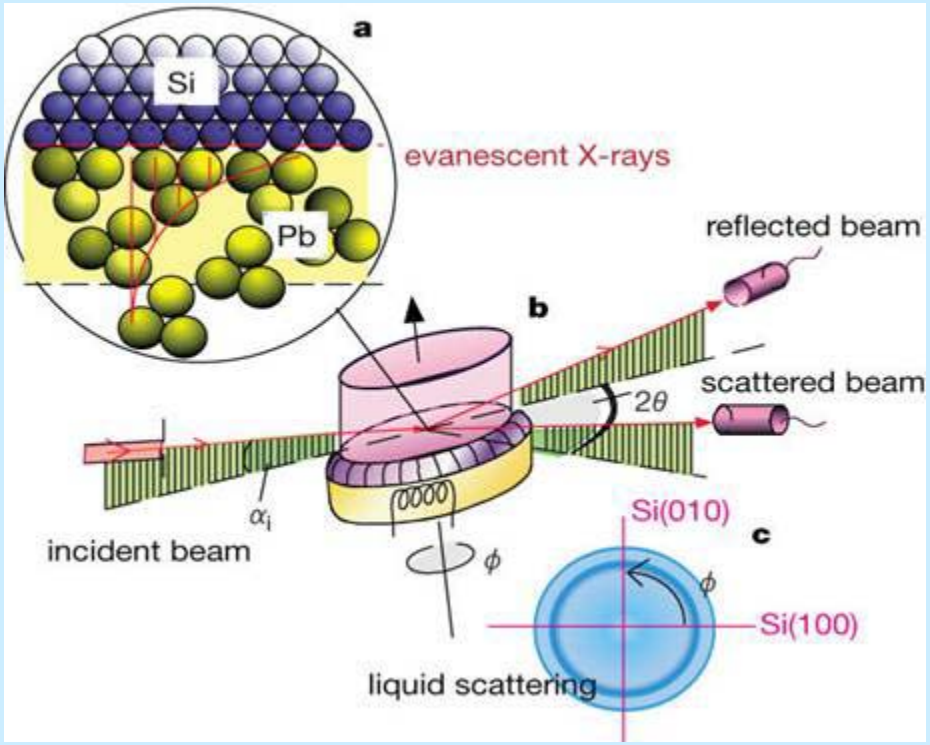
Strong „parasitic“ absorption in the liquid metal and the crystal!

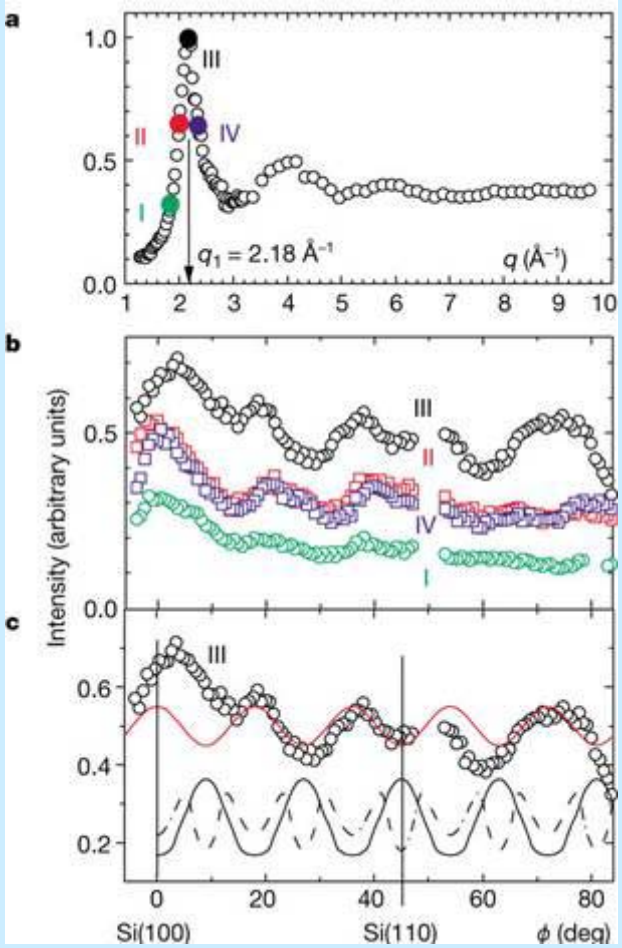
Observation of five-fold local symmetry in liquid lead

Hard X-rays: Large penetration depth!

(Penetration of several cm of material)

collimated beam
(10 μm vert.)
α_i=0.03°





Surface X-ray scattering experiments with high energy (70 keV)

H. Reichert et al., Nature 408 (2000) 839

High energy XAFS

Grazing incidence X-ray absorption spectroscopy at the Pb K-edge (88 keV):

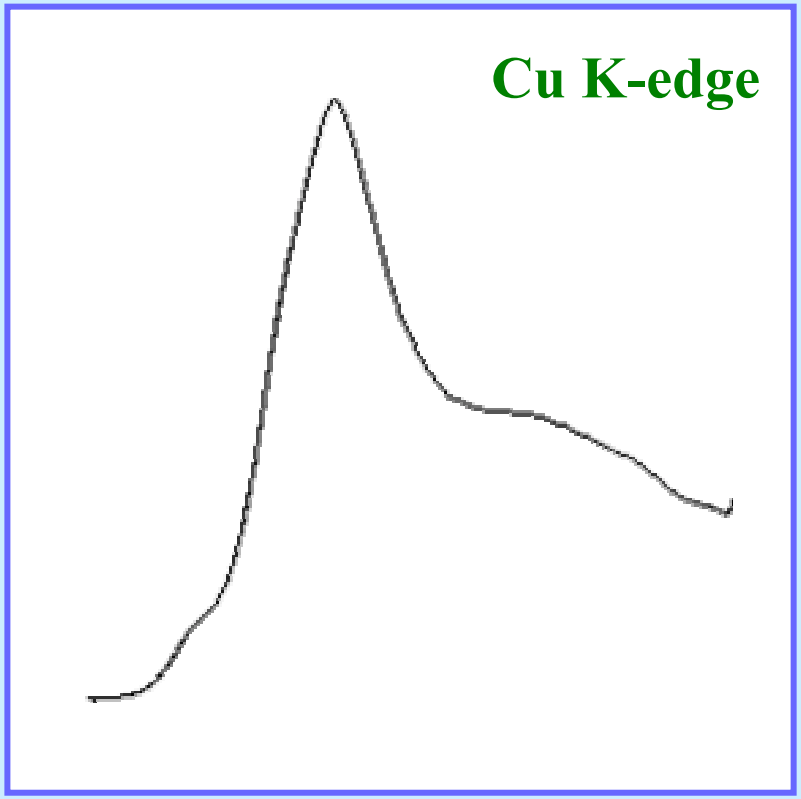
- penetration of the (optical thin) Si-material
- specular reflection at the Pb (liquid) / Si interface
- angle variation allows
  depth profiling of the local structures in the liquid
- temperature variation: surface melting of Pb/Si?

Activation of a $CuO/ZnO/Al_2O_3$ catalyst for methanol synthesis

Goal:

Optimization of the properties of catalysts

At higher energies (Pt K-edge) one can look into e.g. stainless steel cells.

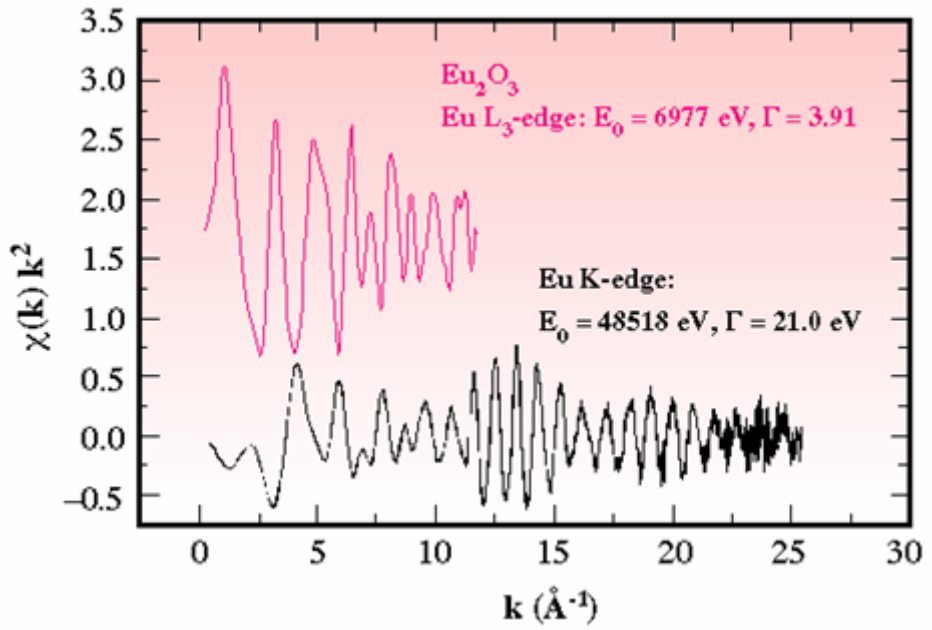


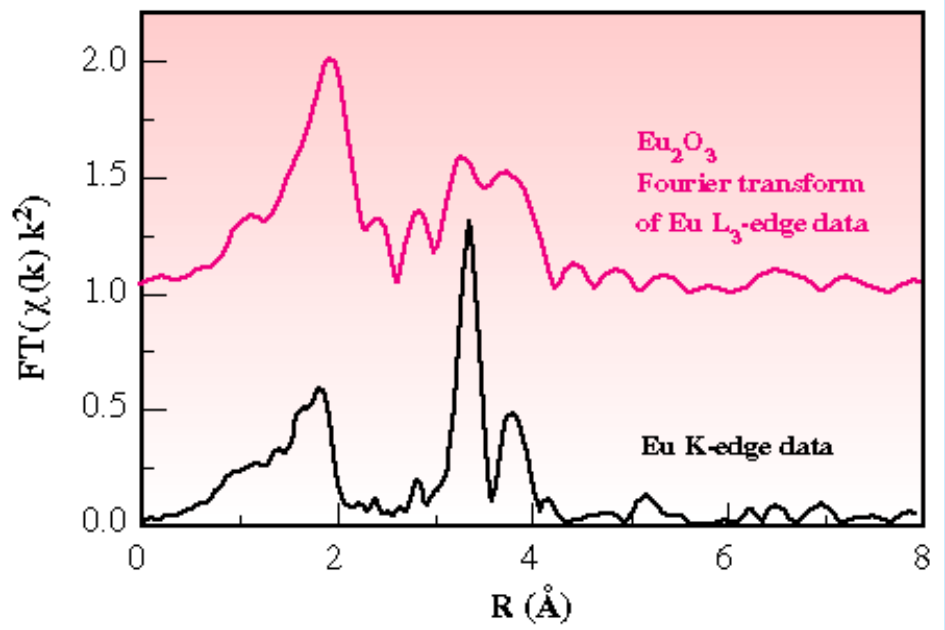
In situ reduction in H_2 atmosphere

Time resolution: **50 ms**

High energy absorption edges

Borowski, D.T. Bowron, S. de Panfilis, J. Synchrotron Rad. 6 (1999) 179





Eu_2O_3-Probe: Eu L_3-Kante (6977 eV) + Eu K-Kante (48518 eV)

^{63}Eu K 48 518 eV

L_1 8 052 eV

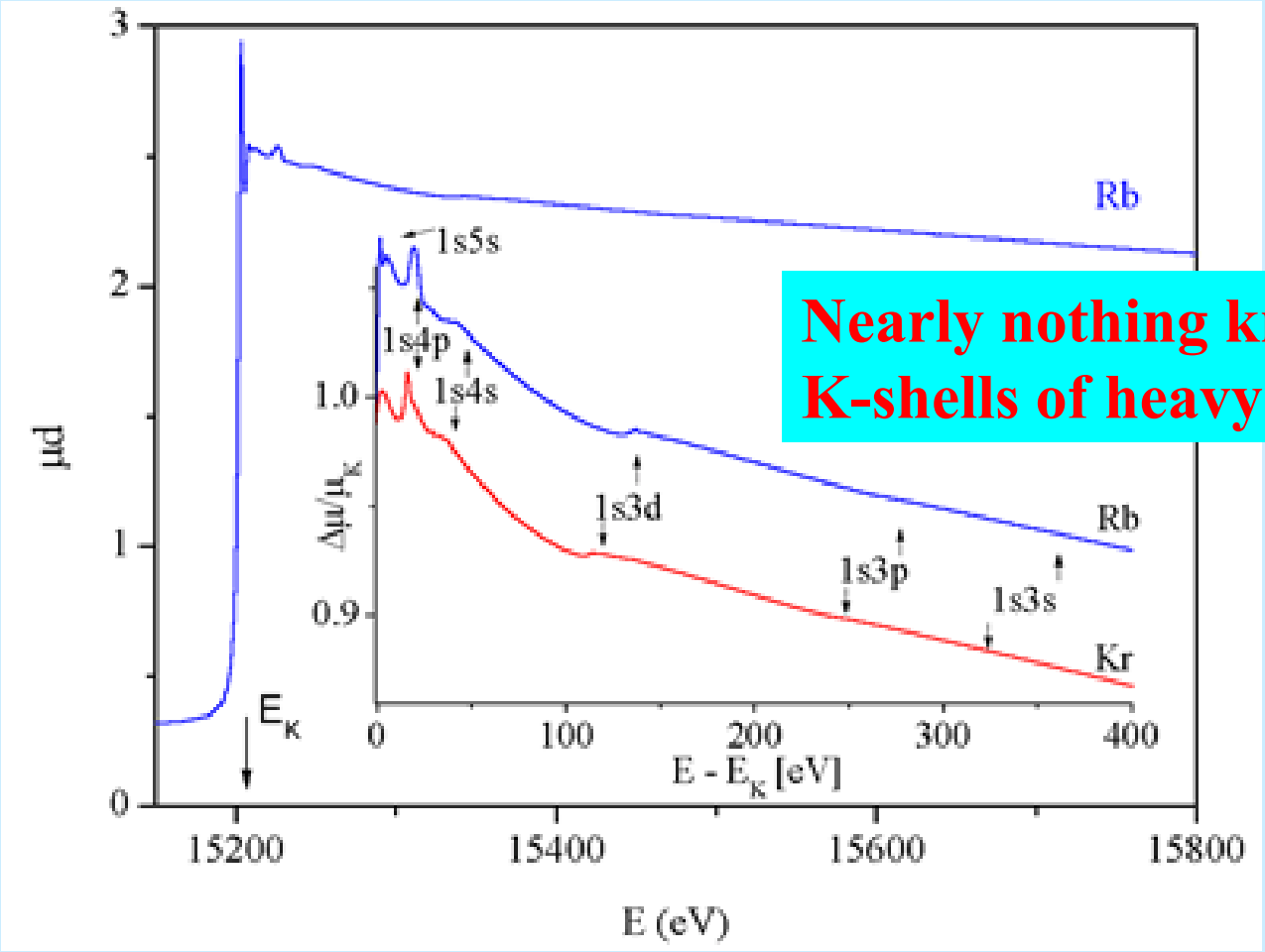
L_2 7 617 eV

L_3 6 977 eV $\Rightarrow$ $\Delta E(L_3\text{-}L_2) = 640$ eV

K-edge data are MUCH better than L_3-edge despite lifetime broadening!

Multishell excitations: Rb und Kr

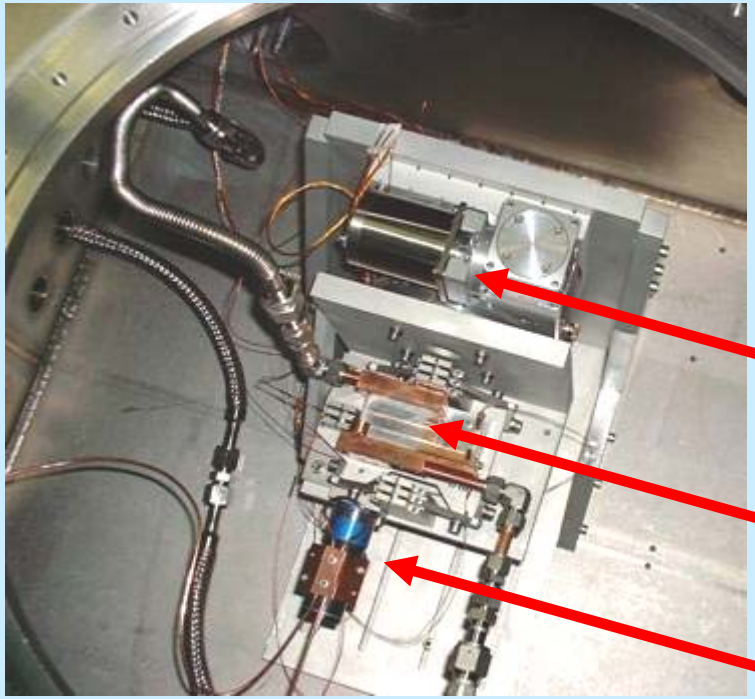
Rb+Kr benachbarte Elemente



Nearly nothing known about K-shells of heavy elements

Kodre, Arčon, Padežnik Gomilšek, Prešeren, Frahm, J. Phys. B: At. Mol. Opt. Phys. 35, 3497, 2002

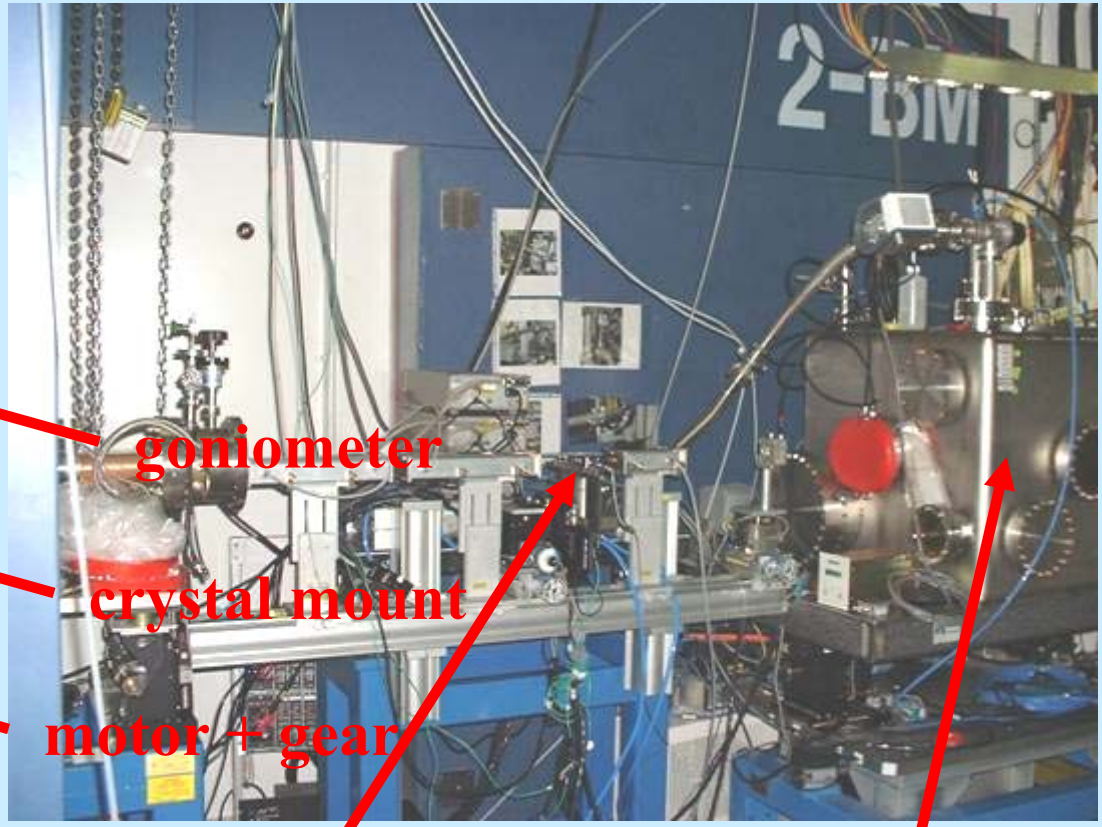
QEXAFS Experiments at the APS undulator 1-ID



goniometer

crystal mount

motor + gear



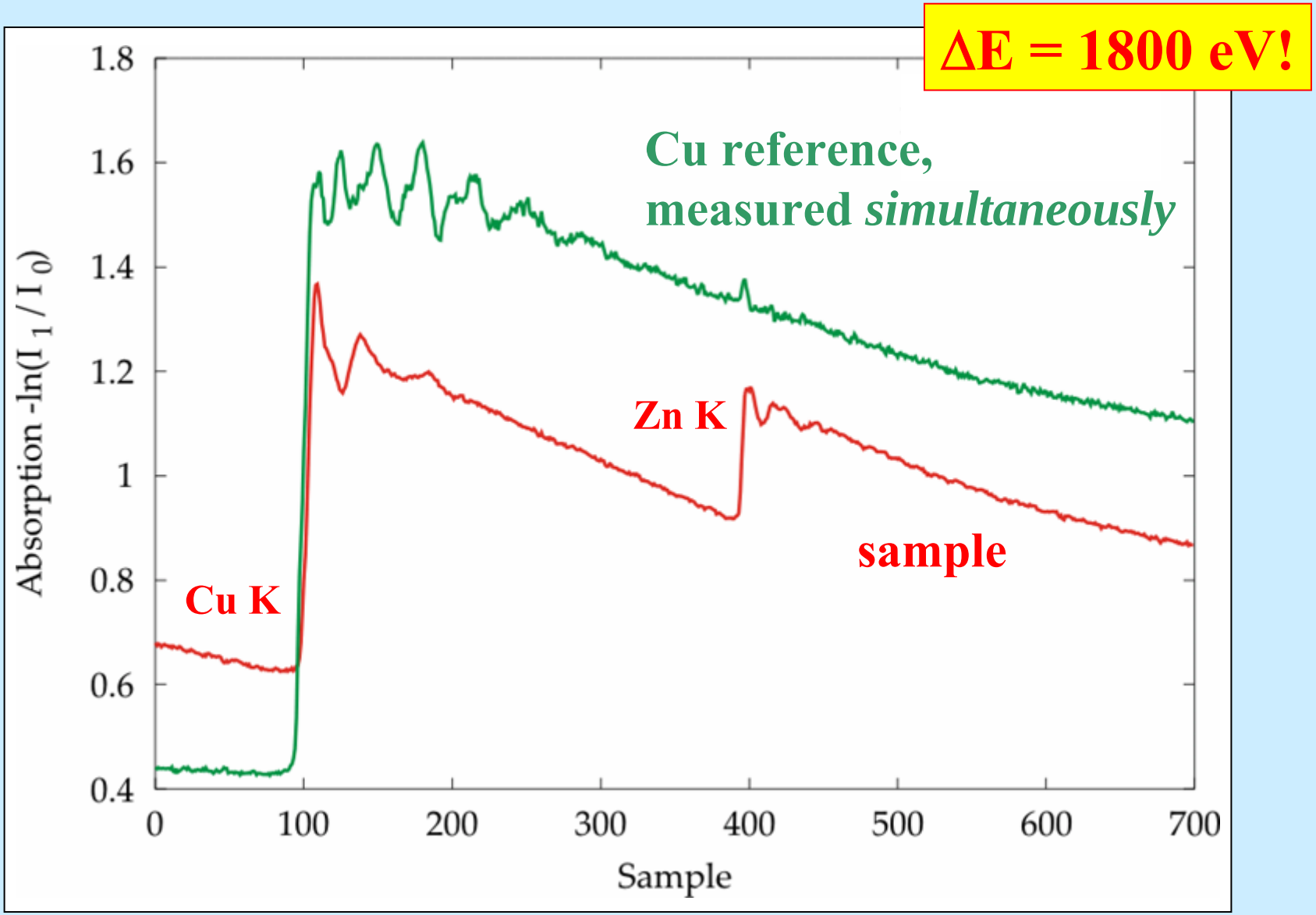
Monochromator (crystal not mounted), cryogenic cooling

Experimental setup

sample

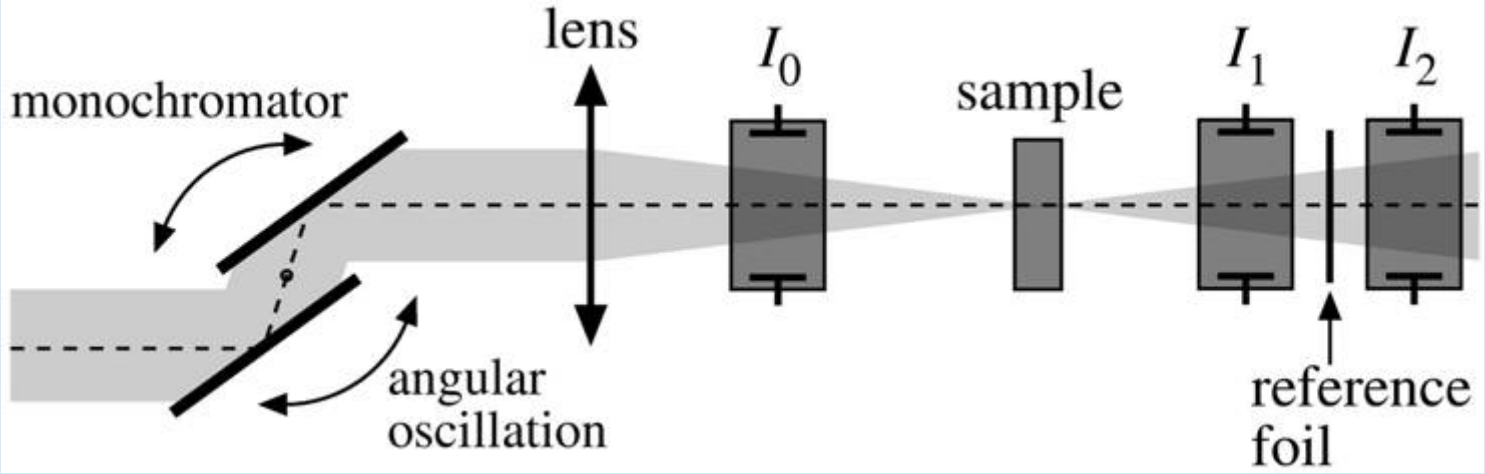
monochromator

CuO/ZnO-catalyst: Single scan, 50 ms

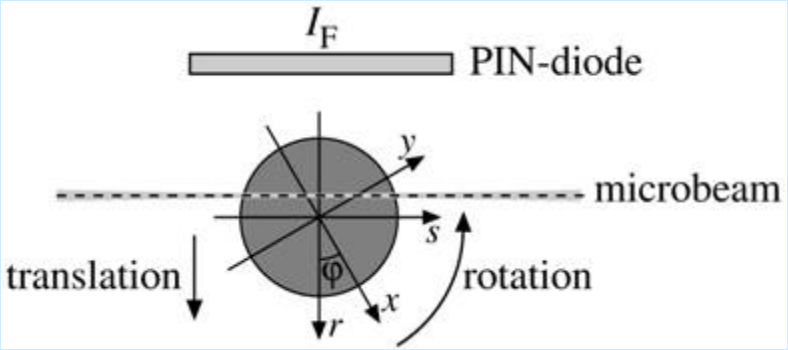


XANES-Tomography

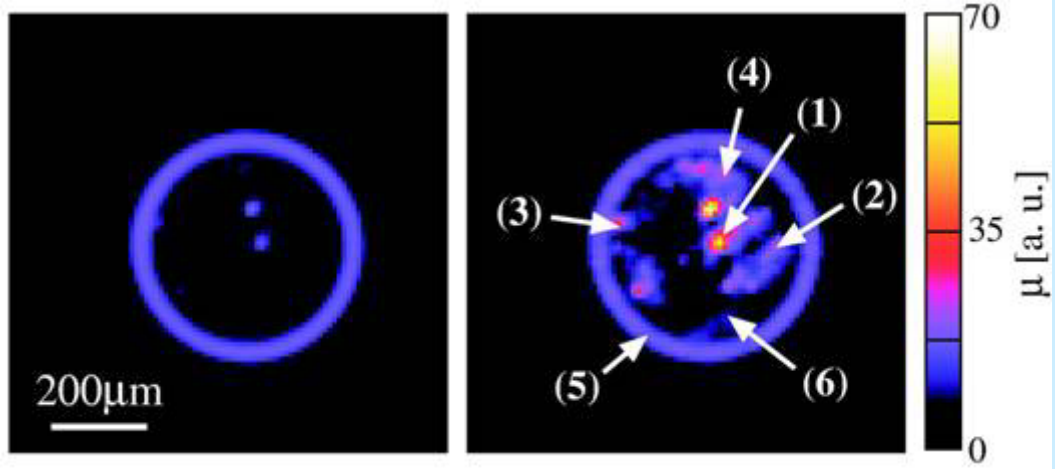
Goal: 3-d Imaging with microscopic resolution



Experimental setup, side view

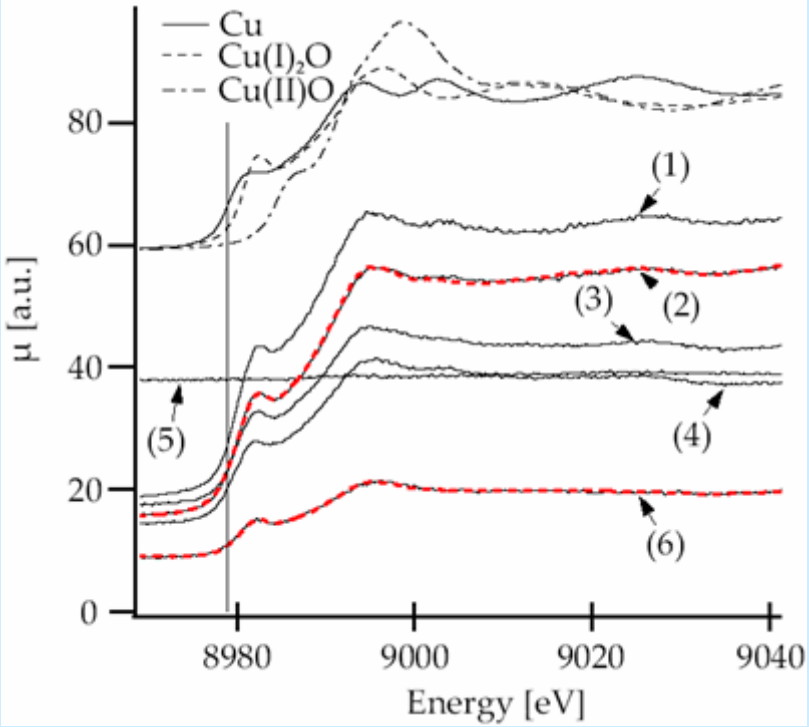


Sample stage, top view



Cu/ZnO catalyst

Sample below / above Cu K-edge



Reconstructed Spectra with reference compounds

Reconstruction at different positions after several oxidation/reduction cycles

Sample in glass capillary, outer diameter 500 mm, inner diameter 400 mm.

Beam size: 10 µm x 10 µm

1s/sample position, 10 Hz

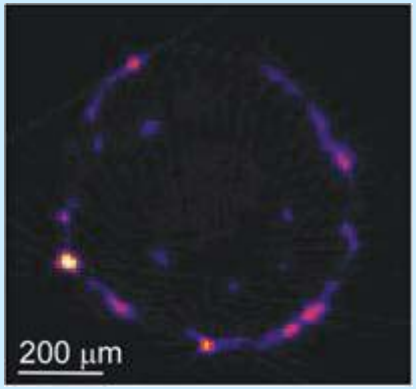
(Appl. Phys. Lett. 2004)

Tomato root grown on a polluted (Zn, Pb) soil

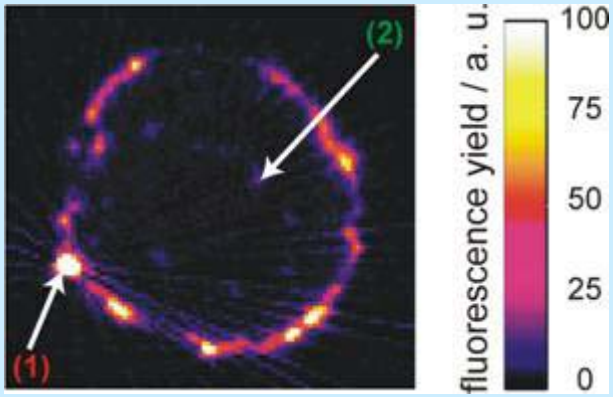
- Low metal-ion concentration (<100 ppm):

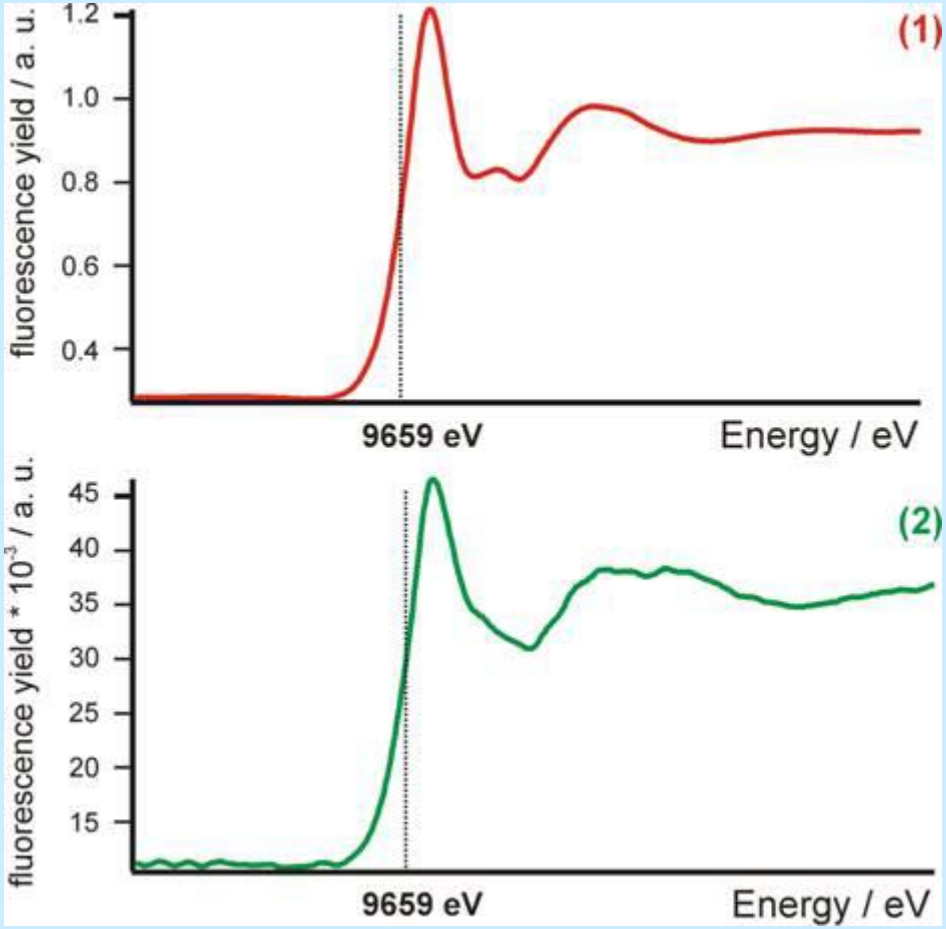
  → Fluorescence tomography at the **Zn K-edge**

Below Zn K-edge



Above Zn K-edge





μ-XAFS at high energies

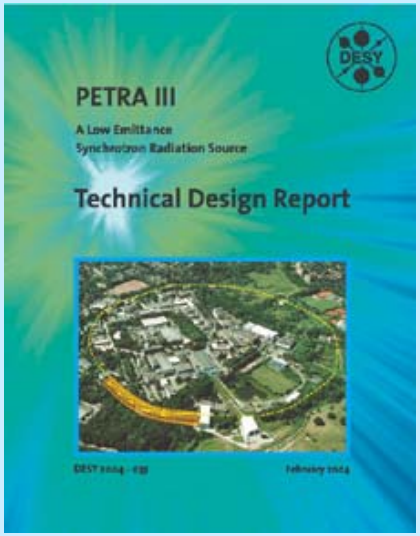
Advantage:

High penetration through sample cells and other materials, e.g. characterization of multicomponent samples on the μm/nm-scale.

=> Valence distribution of elements

Experiments at PETRA III

PETRA III:
A Low Emittance Synchrotron Radiation Source
Technical Design Report
February 29, 2004
(download from www.desy.de)



"The construction work will start in July 2007.
First photons for user experiments are expected in 2009."

Absorption Spectroscopy, Authors and Consultants:

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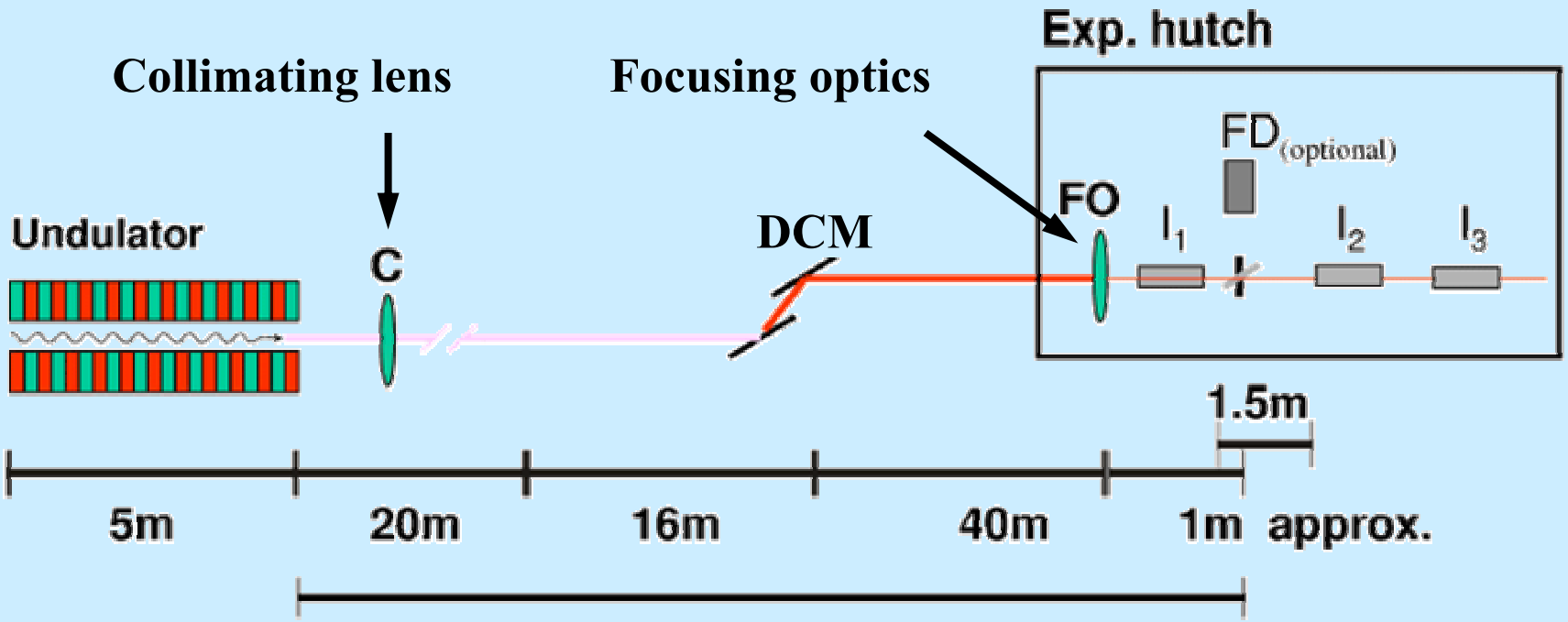
Beamline layout at PETRA III



Absorption beamline at PETRA III for E = 30 - 100 keV

Si(311), Si(511)-crystals,

good energy resolution achievable (few eV).

Reference:

Beamline requirements

Monochromator:

Fast scans for time resolved studies (500 eV/s, basic option)

Insertion device:

Undulator with taper-option necessary to give 1500 eV bandpass

If highest brilliance necessary:

Undulator scanned with monochromator (500 eV/s)

High energy absorption edges

- K-edges: Larger wavenumbers compared to L-edges possible

- K-edges thus more sensitive for disorder

Theory: Van Hung, Ba Duc, Frahm: J. Phys. Soc. Japan 72, 1254 (2003)

- Good penetration of sample cells
  (several mm of metals like Fe, several cm of Si or H_2O)

- But: Larger lifetime broadening of K-XAFS
  $\Rightarrow$ New methods necessary (numerical / experimental)

However: Lifetime broadening seems to be not as critical as expected, already very promising results in literature!

The high energy range offers new scientific possibilities for XAS!

Acknowledgement

BUW: D. Lützenkirchen-Hecht, R. Wagner,
Diploma and thesis students

ETH Zürich: J.-D. Grunwaldt

RWTH Aachen: B. Lengeler, C. Schroer

W. Drube, K. Klementev, HASYLAB, Hamburg

A. Filipponi, University of L'Aquila, Italy

ESRF, Grenoble

APS, Argonne